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PHYSICAL CHEMISTRY, METALLOGRAPHY, AND KINDRED SUBJECTS

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A GENERAL DISCUSSION ON THE PHENOMENA OF POLYMERISATION AND CONDENSATION.

Thursday, 26th September to Saturday, 28th September, 1935.

THE SIXTY-THIRD GENERAL DISCUSSION OF THE FARADAY SOCIETY (being the fourth Colloid Meeting organised by the Colloid Committee of the Faraday Society, which comprises representatives of the Royal Society, the Biochemical Society, the Chemical Society, the Faraday Society, the Physical Society, the Physiological Society, and the Society of Chemical Industry), was held in Cambridge from the 26th to 28th September, 1935, inclusive.

The subject under discussion was "The Phenomena of Polymerisation and Condensation," the papers being considered under the two main headings: (1) General and (2) Special.

The meeting was held in the Zoology Department of the University of Cambridge by courtesy of Professor Stanley Gardiner, the President Mr. W. Rintoul occupying the Chair throughout the meeting. By the courtesy of the Master and Fellows, members and guests were accommodated in Pembroke College, a considerable overflow staying, however, at the Bull Hotel. Those staying at the Bull Hotel were able to join the party in College for meals. Morning coffee and afternoon tea were taken in the Department of Zoology.

The Guest Night Dinner was held on Friday, 27th September, in Hall. There were no formal speeches, but the toast of the overseas guests was proposed by Professor Donnan and replies by Professor Staudinger, Professor Kurt Meyer, Professor Mark, Professor Katz and Dr. Carothers were called for. The toast of the Master and Fellows of Pembroke College was proposed by the President and Mr. S. C. Roberts replied. Toasts were also accorded to Professor Rideal and Mr. Wansbrough-Jones.

At the Inaugural Meeting the Vice-Chancellor of the University, Mr. J. F. Cameron (the Master of Caius and Gonville) welcomed the Society to Cambridge and took the opportunity of paying a tribute to the memory of Sir William Hardy on whose initiative the Colloid Committee of this Society was formed. The President then introduced the overseas guests, members and visitors and called upon them each to rise in his place, whereupon they were welcomed with acclamation. Those so welcomed were: Dr. L. Altwegg (*Paris*), Dr. E. Bergmann (*Rehoboth*), Dr. J. H. de Boer (*Eindhoven*), Dr. T. F. Bradley (*Linden, N.J.*), Dr. W. H. Carothers (*Wilmington Del.*), Dr. H. Dostal (*Wien*), Dr. F. Eirich (*Wien*), Dr. R. Houwink (*Eindhoven*), Professor and Mrs. J. R. Katz (*Amsterdam*), Mr. and Mrs. R. H. Kienle (*Bound Brook, N.J.*), Professor P. N. Kogerman (*Tartu*), Frln. Dr. D. Kruger (*Berlin*), Professor H. Mark (*Wien*), Professor M. Mathieu (*Paris*), Professor Kurt H. Meyer (*Genthod-Genève*), Dr. R. Meyer (*Paris*), Dr. J. van der Minne (*Amsterdam*), Dr. Orthner (*Frankfurt*), Dr. J. C. Patrick (*Yardville, N.J.*), Professor H. Pringsheim (*Prag*), Dr. E. Proskauer (*Leipzig*), Dr. G. Salomon (*Zurich*), Dr. Sauter (*Freiburg i. Br.*) Professor and Mrs. Signer (*Bern*), Professor H. Staudinger (*Freiburg i. Br.*), Professor

T. Takei (*Tokyo*), Dr. P. von Tavel (*Bern*), Dr. J. C. Vlughter (*Amsterdam*), Professor H. I. Waterman (*Delft*), Dr. A. Weidinger (*Amsterdam*), Professor F. Weigert (*Leipzig*), Dr. H. B. Weiser (*Houston, Tex.*).

Professor E. K. Rideal then said: In the first place I would like to thank, both on your behalf and personally, our Vice-Chancellor for devoting the time to open our discussion. To those of you who are not acquainted with our University I can give the assurance that the Vice-Chancellor is our busiest representative.

I wish also to extend a cordial invitation to those present to inspect the laboratory of Colloid Science. It is a relatively small laboratory, but we have attempted to make it a convenient and pleasant place to work in.

Finally I would like to draw your attention to the fact that the scientific works of the founder of the Colloid Committee of the Faraday Society, Sir William Bate Hardy, F.R.S., will be published shortly by the Cambridge University Press, who have provided us with a number of sample partly-printed copies for inspection. As some of you may remember, the cost of publication has been estimated at about one thousand pounds; towards which the Cambridge University Press have most generously provided three hundred pounds. I have to thank Hardy's College, Gonville and Caius, the Royal, Physiological, Chemical, Biochemical and our own, the Faraday, societies, the dominions of South Africa, Australia, and New Zealand, and particularly the Premier of the latter, for interesting themselves in this matter. I would also like to express my indebtedness to Lady Hardy and Dr. E. C. and Mrs. Smith, for their valuable assistance in the collecting of the papers.

I trust that we as a Society shall welcome this publication, which as you well know contains a numbers of papers classic in our science.

At the conclusion of the meeting a vote of thanks was accorded at the instance of the President to the overseas guests, whose presence had particularly contributed to the success of the meeting. Professor Kurt Meyer replied on behalf of the overseas guests, and said that they would all be very glad to come again to meetings of the Society. On the motion of the President a vote of thanks was accorded to Professor Gardiner and the staff of the Department. The Secretary proposed a vote of thanks to the Master and Fellows of Pembroke College and mentioned the great difficulties under which the College was labouring owing to the recent death of three senior Fellows and, only ten days ago, of the Bursar, Mr. H. G. Comber. They would all, he knew, endorse his action in writing to the Master and expressing the Society's sympathy with the College. The smooth way in which the arrangements for their comfort had been carried out reflected great credit on the servants of the College and those Fellows who had carried on its work. This was received with sympathy. The President also proposed votes of thanks to the contributors of papers, to Dr. Rabinowitch for his translations, and to the Colloid Committee and the sub-committee, particularly Professor Rideal, for organising and arranging the meeting. The proceedings closed with a vote of thanks to the President and the Secretary.

The report of the meeting, including all the papers contributed and the general discussion thereon, appears in the following pages :

is identical with the curve (curve *b*) for the van der Waals attractive energy, for distances greater than 4 Å., and while further it is assumed, on the basis of data for other molecules⁴⁸ that, when the equilibrium distance, i.e., the position of the potential minimum lies at 3.7 Å, the energy content is again zero at 3.4 Å. In the calculation (curve *b*) the van der Waals reciprocal energy is set equal to $\frac{C}{r^6}$, whereby

C is calculated according to the Slater-Kirkwood approximation formula when an average value $\alpha_0 = 1.7 \times 10^{-24}$ is taken for the polarisability. Thus

$$C = 805 \times 10^{-48} \text{ kg. cal. } \times \text{ cm.}^6$$

If we let the two benzene rings approach each other along a line perpendicular to both rings, then the six CH groups which are closest to each other (the pairs 1-1', 2-2', etc. in Fig. 4 will be in unfavourable positions with respect to the anisotropy of the polarisability. In order to take this into account, we use the formula mentioned in § 3:

$$C = \alpha_0^2 (\alpha_a^{3/2} - \alpha_b^{3/2} + 4\alpha_c^{3/2}) \frac{h\nu_0}{8}$$

for which we calculate $h\nu_0$ by substituting for C the value of C according to the approximation formula of London, $C = \frac{3}{2} \alpha_0^2 h\nu_0$ and for S the experimental value ($S = 10.67$ kg. cal./mol) in the expression

$$S = \frac{0.0277}{2} C \quad (\text{cf. § 5}).$$

We thus obtain $h\nu_0 = 353$ kg. cal. In Fig. 15, curve *a* represents the respective reciprocal energy of the six pairs of CH groups which lie opposite each other, calculated with the aid of a value of C which takes into account the anisotropy ($C = 592 \times 10^{-48}$ kg. cal. \times cm.⁶), while curve *b* gives the total reciprocal energy of both benzene molecules, whereby, as in § 3, no account is taken of the anisotropy for pairs of CH groups, which do not

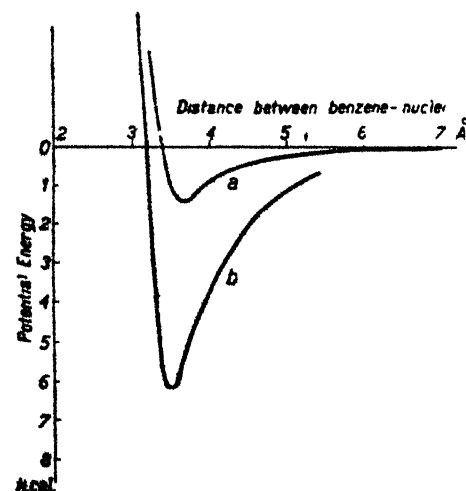


FIG. 15—Potential energy of two benzene molecules, lying in parallel planes, as a function of the distance between the molecules (curve *b*). Curve *a* represents the reciprocal energy of the six pairs of CH groups which lie opposite each other.

lie opposite each other ($C' = 770 \times 10^{-48}$ kg. cal \times cm.⁶). Although,

⁴⁸ Cf. table in H. A. Stuart's *Molecular Structure*, Berlin, 1934, pp. 36 and 262.

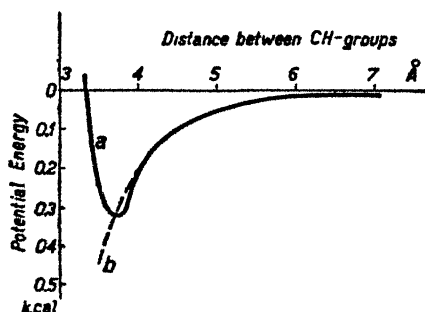


FIG. 14—Potential energy of two aromatic CH groups as a function of the distance between the groups (curve *a*). Curve *b* gives the course of the van der Waals attractive energy.

therefore, at distances slightly less than 3.7 Å. the pairs of CH groups directly opposite each other are situated upon the repulsion branch of the potential curve, the molecules taken as a whole nevertheless attract each other with increasing force until the potential minimum for the whole molecules is reached at 3.5 Å. It is evident, further, that at a mutual separation of 3.2 Å. the energy content is still only slightly negative, while at 3.1 Å. the repulsion is already so great that 3 to 4 kg. cal. would be necessary to cause the molecules to approach to this distance.

Therefore, if two or more benzene rings in a molecule must be brought so close to each other, this occurs at the cost of the energy content of the molecule. It may be that the easy dissociability of hexaphenyl-ethane into two triphenyl-methyl radicals is partially due to this effect. In this case the energy of dissociation is about 12 kg. cal., while on the contrary 71 kg. cal. are necessary to separate two normally bound aliphatic carbon atoms.⁴⁷ We must keep this repulsion strictly in mind in the discussion of the orientation in polystyrene.⁴⁸

15. Positions of the Benzene Rings in Polystyrene, Assuming a Structure of the Aliphatic Carbon Chain like that in Solid Paraffins.

If we assume that the aliphatic carbon chain in polystyrene has the same structure as the aliphatic chains in the solid paraffins, and if we imagine the phenyl groups substituted on the carbon atoms 0, 2, 4, etc., then we may distinguish several cases A, B, and C.

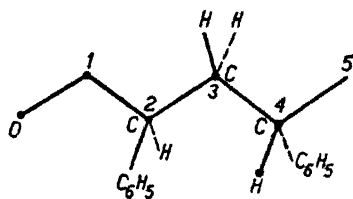


FIG. 16.—Part of a polystyrene molecule; the C_6H_5 group on the second and the H atom on the fourth carbon atom of the chain stick out from the figure; the H atom on the second and the C_6H_5 group on the fourth carbon atom lie behind the plane of the drawing.

A. The phenyl groups on the second and fourth carbon atoms are situated on different sides of the carbon chain. This is indicated schematically in Fig. 16 in which the C_6H_5 group on the second, and the H atom on the fourth carbon atom must be imagined to stick out from the figure and the H on the second and the C_6H_5 on the fourth carbon atom must be imagined to lie behind the plane of the drawing. We consider the three following

positions under this case :

- That in which both benzene rings lie perpendicular to the direction of the carbon chain (Fig. 17).
- That in which both benzene rings lie parallel to the direction of the carbon chain (Fig. 18).
- That in which one of the benzene rings is perpendicular and one parallel to the carbon chain (Fig. 19).

⁴⁷ In the case of still larger aliphatic groups, naphthyl, etc., the dissociation is still easier.

⁴⁸ Additional phenomena, connected with the repulsion between two phenyl groups which are very close to each other in the molecule, are the stretched-out form of diphenyl, and the relatively large valence angle ($142^\circ \pm 8^\circ$) of diphenyl ether.

If we keep in mind that, in all positions (especially in position *A c*, Fig. 19), the CH groups of the benzene rings which have approached closest to each other, do not attract each other with the maximum force, but even repel each other appreciably, we come to the conclusion that the benzene rings attract each other in all three positions and that binding energies are :

Position *A a* about 2.4 kg. cal.

" *A b* " 2.3 "

" *A c* " 1.8 "

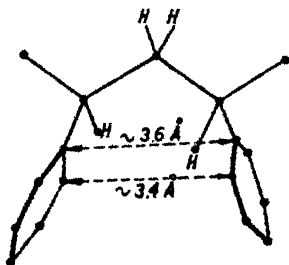


FIG. 17.—Part of a polystyrene molecule; positions as in Fig. 16; both benzene rings perpendicular to the direction of the carbon chain.

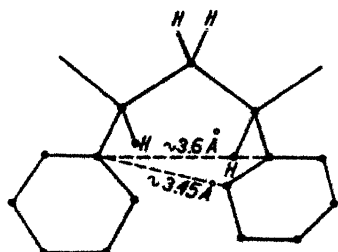


FIG. 18.—Part of a polystyrene molecule; positions as in Fig. 16; both benzene rings parallel to the direction of the carbon chain.

If, further, we remember that in position *A b* the distance between the H atom, which is also attached to carbon atom 4, and the closest CH group of the benzene ring attached to carbon atom 2 is only about 1.8 Å. (calculated to the nucleus of the C atom of the CH group. If the H atom is calculated separately the repulsion becomes still much greater), we see that the combining energy in position *A c* and especially in position *A b* will thereby be much smaller than the above-mentioned quantities indicate (the energy content of the system of two H atoms and two benzene radicals will probably even be positive in these positions because of the strong repulsion between the H atoms and the closest CH groups of the benzene nuclei).⁴⁹

The differences in energy among the three above-mentioned positions therefore become greater than the average kinetic energy at room temperature, so that we arrive at the result that case *A a* is not only by far the preferred one, but also that the benzene radicals, in the cases of linkages which fall under case *A*, will execute oscillations about position *A a*.

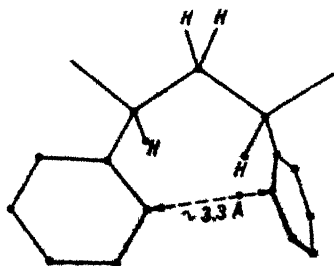


FIG. 19.—Part of a polystyrene molecule; positions as in Fig. 16; one of the benzene rings parallel and the other perpendicular to the direction of the carbon chain.

⁴⁹ Up to now we have worked only with CH, CH₂, etc., groups and not with individual H atoms. We might continue this practice, and we must then say that the distance between the closest CH groups of the benzene radical attached to carbon atom 2, for example (in position *A b* or *A c*) is only about 2.6 Å. away from CH group 4, so that these two groups will exhibit a strong repulsion.

B. The phenyl groups attached to the second and fourth carbon atoms are situated on the same side of the carbon chain. Since the distance between carbon atoms 2 and 4 is only 2.54 Å., all orientation leads to repulsion, but that in which the benzene rings both lie perpendicular to the direction of the carbon chain, to the smallest extent. One might imagine that the angle at carbon atom 3 would be forced to greater values than 110° by this repulsion. In the completely stretched state, however, the second and fourth carbon atoms are still 3.1 Å. away from each other, so that with parallel orientation the phenyl groups still repel each other slightly. In this latter case the energy content of this grouping would be strongly positive because of the energy necessary for the widening of the angle at carbon atom 3 (this energy would be of the order ⁵⁰ of magnitude of 15 kg. cal., while the repulsion would add 3 to 4 kg. cal. more).

C. The phenyl groups attached to the second and sixth carbon atoms are situated on the same side of the carbon chain. The position in which the benzene rings lie parallel to the carbon chain leads here also to a repulsion, since the distance between the closest CH groups is only 2.58 Å. If both benzene rings are oriented perpendicular to the carbon chain, they attract each other (binding energy about 1.1 kg. cal.), while the most favourable position is that in which one benzene ring is perpendicular and the other parallel to the carbon chain (binding energy about 2.5 kg. cal.). This position is, however, unfavourable as regards the phenyl group attached to the intermediate carbon atom 4 (see under A).

Summarising, we come to the conclusion that when the aliphatic carbon chain is similar to that found in the solid paraffins, the most favourable position of the phenyl groups is that in which they lie alternately to the right and to the left of the chain and perpendicular to the direction of the chain. This is, however, only possible when the other, equally possible stereoisomers cannot be formed during polymerisation. If these latter are formed, and if the chain form is also retained, then the benzene rings certainly lie perpendicular to the direction of the chain, and a weaker spot occurs at that point in the chain.

16. Positions of the Benzene Rings in Polystyrene, Assuming Another Structure of the Aliphatic Carbon Chain.

Another possibility is, however, that when the two phenyl groups on carbon atoms 2 and 4 lie on the same side of the chain, the chain will take another form. If one rotates the groups attached to carbon atom 3 about the line joining 2 to 3 by 180° , for example, the configuration of Fig. 20 results. In this case the groups attached to carbon atom 4' will be repelled by the two H atoms on carbon atom 1, but in any case the benzene ring will again take up a position perpendicular to the direction of the chain.

If only these of all possible stereoisomers should occur one might imagine a chain as in Fig. 21. The benzene rings would certainly all be perpendicular to the direction of the chain (the closest CH groups are then about 3.5 Å. apart) so that a strong attraction prevails between the phenyl groups; the intermediate CH_2 groups, however, exercise a strong repulsion).

⁵⁰ Cf. H. A. Stuart, *Molekülstruktur*, Berlin, 1934, pp. 85, 86.

Another possibility may also be reviewed, *viz.*, that whereby the carbon chain is wound in a spiral, so that the seventh carbon atom comes above the first, etc. Because of the van der Waals reaction between the members of the chain themselves, they will have a tendency to seek a mutual separation of about 4 to 4.5 Å. The benzene rings must then be perpendicular to the axis of the spiral.

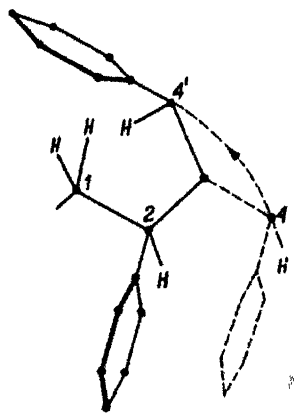


FIG. 20.—Part of a polystyrene molecule; when the two phenyl groups on carbon atoms 2 and 4 lie on the same side of the chain another form of the chain is possible. In reality a position between the two here denoted is very probable.

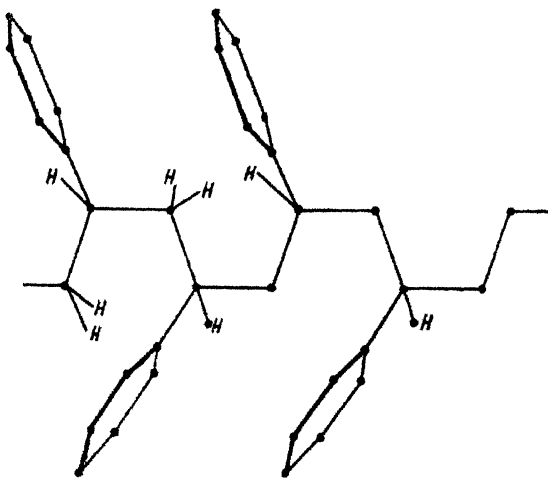


FIG. 21.—A repetition of the positions given in Fig. 20.

17. Conclusion.

We may expect that various configurations of polystyrene occur due to the various possible stereoisomers in different parts of the carbon chain. Common to all these configurations, however, will be a preference of the benzene ring to take up a position perpendicular to the carbon chain, or at least to execute oscillations about equilibrium positions, in which the benzene ring is perpendicular to that direction. If we remember that the polarisability of benzene in the direction perpendicular to the plane of the ring is only about half that in the plane of the ring, we see that an anisotropy will be present in the polystyrene chain, which will completely dominate that of the carbon chain itself. The carbon chain itself would cause an anisotropy such that the polarisability in the direction of the chain would be greater than in the perpendicular direction. Because of the benzene rings which lie perpendicular to the chain, however, the former anisotropy of the chain itself will be more than compensated for and we obtain the smallest polarisability in the direction of the chain, and therefore also the smallest index of refraction. In our opinion herein lies the explanation of the strongly negative double refraction caused by flow of polystyrene,⁵¹ which must be ascribed to the individual polystyrene molecules.⁵²

⁵¹ R. Signer, *Z. physikal. Chem.* 1930, 150A, 257.

⁵² R. Houwink, *Physikalische Eigenschaften und Feinbau von Natur- und Kunstharzen*, Leipzig, 1934, pp. 155, 165.

Summary.

PART I.

The question of the mutual orientation of molecules under the influence of van der Waals' forces is discussed. In general there are two opposing factors, namely: the tendency of the atoms to gather as many neighbours as possible, and the anisotropy of the polarisability. The first of these tendencies practically always dominates over the second. This fact is illustrated with reference to two benzene molecules. In the calculation of the reciprocal energy in the equilibrium state, good results are by chance obtained when use is made of the approximation formula of London or of Kirkwood and Slater, and when the influence of the repulsive forces is neglected. The sublimation energy of benzene, for example, may be satisfactorily calculated in this way.

PART II.

The theoretically calculated value of the tensile strength of common salt is very much greater than the value found experimentally. In the theoretical calculation the influence of the van der Waals forces has been thus far neglected. When this is not done, the theoretical value obtained is still much greater, about 400 kg./mm.². If a secondary structure is assumed, such as has been proposed by Zwicky, and if it is likewise assumed that there are no electrostatic forces of any description between the "blocks," the value obtained for the theoretical tensile strength is still much too great. In this case the value obtained is > 20 kg./mm.², while the experimental value is 0.6 kg./mm.². This low experimental value must be ascribed to a notch effect arising from defects in the lattice, and not to a regular secondary structure.

In the case of artificial resins of the phenol-formaldehyde type and the *m*-cresol-formaldehyde type similar relations between calculated and observed values are encountered. If such an artificial resin is completely polymerised throughout its whole mass and all the C—C linkages possible are actually formed, the theoretical tensile strength may be calculated to be about 4000 kg./mm.². If (irregular) "blocks" are assumed in this case also, and if these blocks are assumed to cohere only by means of van der Waals forces, then the theoretical value of the tensile strength is about > 35 kg./mm.². The experimental value is, in this case as with sodium chloride, very much smaller, *viz.*, about 7.8 kg./mm.² for the phenol-formaldehyde resin, so that here also an influence of a notch effect is probable. On the other hand, in the case of well-oriented cellulose derivatives, the correct order of magnitude for the tensile strength may be obtained by theoretical calculations.

Young's modulus of elasticity is also dependent on the van der Waals bonds present in the artificial resin.

PART III.

The potential curve for the bond between two benzene molecules is examined on the basis of the effects due to the individual CH groups. When the minimum lies at 3.5 Å., the energy content at a separation of 3.2 Å. is only slightly negative, while at 3.1 Å. the repulsion is already so great that 3 to 4 kg. cal. would be necessary to cause the molecules to approach to within this distance.

The relative positions of the benzene rings in polystyrene are investigated, and the conclusion may be drawn that there will be a preference on the part of the benzene ring to lie perpendicular to the direction of the aliphatic carbon chain. This makes understandable the strongly negative double refraction caused by flow.

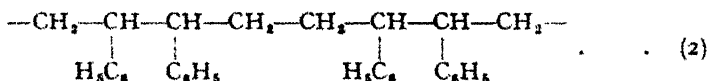
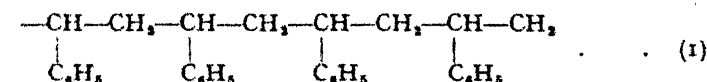
Many thanks are due to Mr. G. Heller for his valuable suggestions concerning Part I. Part II. owes its existence to several discussions with Dr. R. Houwink, and I am greatly indebted to him for his kindness in putting his experimental figures at my disposal.

(*Natuurkundig Laboratorium der N. V. Philips,
Gloeilampenfabrieken,
Eindhoven-Holland.*)

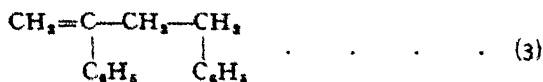
GENERAL DISCUSSION

Professor J. E. Lennard-Jones (*Cambridge*) said: While I agree that Van der Waals' fields play an important rôle in the phenomena discussed by Dr. de Boer and that it is very desirable to estimate their magnitude, I should like to ask the author whether he thinks the theory sufficiently developed at present to make reliable quantitative calculations. I think the formula given by London was intended only for spherically symmetrical systems and even for them it is only approximate. While it gives the right order of magnitude for the inert gases, it is not yet certain that there is not an error by a factor of two. But the error may be greater in the case of aromatic molecules owing to their lack of symmetry and to their special electronic structure in that they contain "non-localised" electrons. Is it not likely that these will require special treatment?

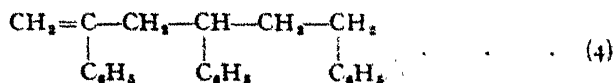
Professor H. Staudinger (*Freiburg i. Br.*) said: The question whether in the polystyrene molecule, the single styrene molecules are linked according to formula 1 or formula 2 is answered in favour of formula 1 by the following experiments: "



Polystyrene, as is well known, depolymerises very easily, reforming chiefly the monomer, but also some dimer, trimer and higher polymers. The yield of the latter products can be increased by performing the depolymerisation *in vacuo*. The formula of the dimer is



and that of the trimer



It follows that formula 1 and not formula 2 must be attributed to polystyrene. Decomposition products which should occur in the decomposition of a product of the formula 2 could not be observed.

However, as was originally supposed, the constitution of the polystyrenes is more complicated. According to viscosity measurements, products prepared with the aid of catalysts have the constitution of formula 1, for in this case determinations of the molecular weights cryoscopically and by viscosity measurements agree well. The end groups of these molecules remain, however, unknown. The meso- and eucolloidal polystyrenes

⁵⁴ Compare H. Staudinger and A. Steinhöfer, *Annalen*, 1935, 517, 35.

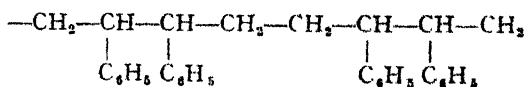
obtained by heat polymerisation have a more complicated structure than the hemicolloidal; the molecular weight determined by the viscosity method is smaller than that given by Svedberg's method,⁵⁴ and by the osmotic method.⁵⁵ In this case unknown branching must have occurred in the formation of the high polymer. By increased temperature of polymerisation these side reactions take place to a greater extent. For this reason it will be difficult to make final calculations on the relations between the size of the molecules and the tensile strength, unless the structure of the molecules is previously elucidated.

Professor K. H. Meyer (*Genève*) said: De Boer has calculated the modulus of elasticity of an artificial phenol-formaldehyde resin with only primary valencies. The value of 11,000 kg./mm.² found is far beyond the observed value.

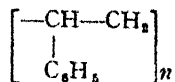
Lotmar and I recently calculated the modulus of a cellulose-chain according to our spacial model, taking into account both the valency-oscillations and the deformation-oscillations (*Knickschwingung*). The calculated value was $10,000 \pm 2000$ kg./mm.² We measured the modulus of well-orientated natural cellulose fibres by an acoustic method, and found that all the fibres tend to a value of about 11,000 kg./mm.² This experiment is certainly the most direct proof in favour of the primary valency chain formula of cellulose.

Dr. J. H. De Boer (*Eindhoven*), said, in reply to Professor J. E. Lennard-Jones: It is perhaps possible that some other attractive forces are present in the reciprocal action of two benzene molecules; indeed benzene molecules are not directly comparable with inert gas atoms or with aliphatic hydrocarbons, as they have one electron per C-atom left. But, on the other hand, we see that the same procedure which leads to the right order of magnitude of the heats of sublimation of the inert gases, hydrogen, oxygen, nitrogen, aliphatic hydrocarbons and the like, leads to the right value for the heat of sublimation of solid benzene.

In reply to a question by Dr. J. R. Katz: The distance of 10 Å. in polystyrene resulting from the X-ray investigations of Dr. Katz has puzzled me too. Perhaps it is related to a distance between two different polystyrene molecules in a special direction. In every case my steric formulae, supplementing the formula of Staudinger and based upon it, allow the distance of 10 Å. to the same extent as the formula of Staudinger does. There are no arguments in favour of the formula:—



In addition to the arguments in favour of the common formula:—



given above by Professor H. Staudinger, I mention the absorption spectrum* of polystyrene which is identical to that of ethyl benzene.

The remark of Professor K. H. Meyer is very valuable; it shows that, as also in the case of the tensile strength, the experimental values found with cellulose fibre fit very well with the values given by theory.

⁵⁴ Compare this vol., No. 18 (R. Signer).

⁵⁵ Compare this vol., No. 6 (H. Staudinger).

* J. H. de Boer, R. Houwink and J. F. H. Custers, *Rec. tr. chim. P. B.*, 1933., 52, 799.

POLYMERS AND POLYFUNCTIONALITY.

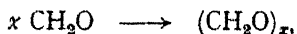
BY WALLACE H. CAROTHERS.

Received 12th July, 1935.

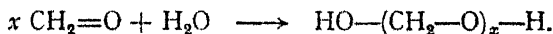
1. Definitions.

The importance of polymerisations is indicated by the title of the present program, and it is a curious fact that little agreement exists concerning the accepted meaning of this term. Text-books, dictionaries, and even recent publications by original investigators,¹ generally state that a monomer and its polymer have identical compositions, and a corollary is that polymerisation consists in pure self-addition, and is peculiar to unsaturated compounds. But it appears that not one of these conditions is necessarily satisfied by reactions that are universally recognised to be polymerisations. Moreover there is little relation between actual usage and text-book definitions.

An accepted polymerisation is the transformation of formaldehyde into polyoxymethylene. The process under some conditions perhaps is



and under others ²

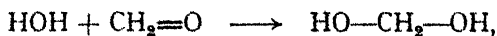


In the latter case for moderately small values of x the composition of the polymer will be very different from that of formaldehyde: at large values of x the difference may be questionably detectable, but the question, of course, is one of fact not definition.

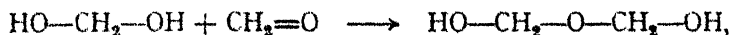
Turning to the mechanism of the process, there are various conceivable possibilities, such as:

1. The polymerisation of perfectly pure and dry formaldehyde might involve opening of the carbonyl bond giving free radicals $-\text{CH}_2-\text{O}-$ whose mutual combination would result in a long chain.

2. In the presence of traces of water, we might have first



a manifestation of formaldehyde's very strong tendency to add ROH. The product here is also ROH, and reaction therefore proceeds



and further similar steps finally lead to a very long molecule.³

3. In aqueous solutions formaldehyde is largely present as hydrates

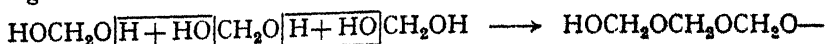


¹ E.g., Staudinger, *Die hochmolekularen organischen Verbindungen*, Julius Springer, Berlin, 1932, p. 10.

² Cf. Staudinger, *loc. cit.*, p. 255.

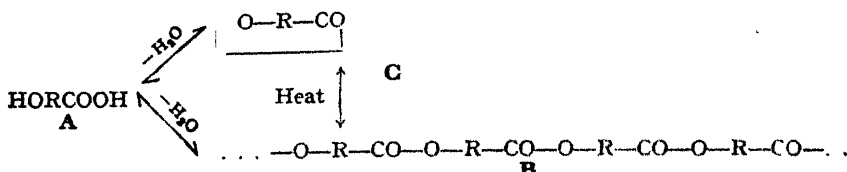
³ Cf. Staudinger, *ref. 1*, p. 10.

Polymer is formed by adding strong acid to such solutions. The reaction might be



i.e., an intermolecular condensation or dehydration.

Further peculiarities are illustrated by polyesters where all of the following transformations can be realised in one case or another.⁴



In many cases the acid can be converted into a polyester under conditions where the monomeric lactone **C** is known to be stable. Moreover, it is then often possible by titration to show that a terminal carboxyl group is present in the ester product in the expected amount. The reaction involved is clearly one of condensation (not self-addition of an unsaturated or cyclic intermediate). Nevertheless, it seems scarcely reasonable or practical to argue that the product is not a polymer. For one thing, such polyesters can generally be transformed under appropriate conditions to the corresponding cyclic monomers (lactones), and the latter can be reconverted to products practically indistinguishable from **B**. In this case the reaction must consist essentially in self-addition. We can hardly say that a compound of the type **B** is a polymer if formed by one method, but not if formed by another. Moreover, there are some cases (*e.g.*, δ -lactones and lactide) where transformation between **B** and **C** occurs so readily that it is difficult or impossible to know which one is the product first formed from the acid. Similar confusion occurs with many reactions involving formaldehyde: it is often impossible to know whether products arise by direct intermolecular dehydration of a methiolol compound or by self-addition of an intermediate methylene compound.

Further illustrations might be offered, but these perhaps are sufficient to show that: the composition of high polymers is not necessarily identical with that of the supposed parent monomers; polymerisations that appear superficially to involve only self-addition may involve preliminary hetero additions, and then actually proceed as condensations (or the reverse may be true); polymerisations are in any event not peculiar to unsaturated compounds (keeping in mind, for example, cyclic anhydrides, esters, acetals, and certain ethers and imines).

It is obvious that definitions need to be revised. It will not suffice to insist merely that usage is frequently wrong. The unfortunate effect of existing discrepancies becomes especially apparent when one reads that a resinification reaction (between an aldehyde and a phenol) doubtless proceeds through an unsaturated monomeric intermediate, because polymerisations are peculiar to unsaturated compounds.

Polymerisations are a special class of reactions, but just how are they distinguished from other intermolecular reactions? Conventionally, they involve the mutual combination of a number of similar molecules,

⁴ Carothers, Dorough, and Van Natta, *J. Am. Chem. Soc.*, 1932, **54**, 761; Carothers and Hill, *ibid.*, 1559; Hill and Carothers, *ibid.*, 1933, **55**, 5031, 5043; Spanagel and Carothers, *ibid.*, 1935, **57**, 929.

but this is not sufficient : the formation of diethyl ether is not polymerisation, and besides we already find references to mixed or hetero-polymerisations where the participating molecules are not all alike.

In the writer's opinion, the essential peculiarity of polymerisations is realised in the statement that they are intermolecular combinations (conventionally, self-combinations) that are functionally capable of proceeding indefinitely (or leading to molecules of infinite size). This may, in fact, be taken as a definition. By way of illustration, referring to the formaldehyde reactions outlined above, it is obvious that, regardless of which of the suggested mechanisms if any may be correct, the functional possibilities are such that any given number of formaldehyde molecules might be combined into a single molecule. The same possibility exists generally with

- (a) unsaturated compounds,
- (b) cyclic compounds and
- (c) polyfunctional compounds generally as, for example, $x-R-y$ where x and y are capable of mutual reaction.

The compounds formally capable of polymerisation then are all polyfunctional compounds. Practically the functions must be such as to permit mutual combination, and polymerisation will then fail only in those relatively rare cases where reaction is exclusively intramolecular. A double bond or a reactive ring will count as a double function.

We may note then that polymerisations do not involve a single unique type of reactivity : they are for the most part merely ordinary reactions made manifold by polyfunctionality, and thus made capable of indefinite continuation in one, two, or three dimensions. But the functions and the mode of their action are generally the same as those already familiar in simple uni-functional compounds (though addition polymerisations of unsaturated compounds certainly present some special peculiarities).

2. The Peculiar Significance of Polymers ; Granular Polymers and Polymerisations in Living Organisms.

The most important peculiarity of high polymers is that they alone among organic materials manifest to a significant degree such mechanical properties as strength, elasticity, toughness, pliability, and hardness.⁵ Weight for weight cellulose and silk are stronger than steel ; rubber exhibits a combined strength and elastic extensibility that is not even remotely approached by anything in the inorganic world while diamond is harder than any other material. The practical uses of high polymers depend almost entirely on these mechanical properties : our clothing and furniture and much of our shelter are made of such materials. The names cellulose, wool, rubber, and silk suggest at once the great importance of the non-chemical uses of natural high polymers.

Probably the bulk of the organic matter in living beings is made up of high polymers. The necessity for this lies in the fact that living organisms must have physical form and coherence, and polymers are the only organic materials capable of supplying these properties. The variability of living matter also requires a high degree of structural

⁵ Cf. Meyer and Mark, *Der Aufbau der hochpolymeren organischen Naturstoffe*, Akademische Verlagsgesellschaft, Leipzig, 1930.

complexity, and the possibilities of high polymers in this connection are indicated by Fischer's well-known calculation that 20 different amino acids may form 2.3×10^{18} different polypeptides of 20 units. Another pertinent fact is that the physical properties of high polymers are profoundly affected by their physical history: the melting-points of certain polyesters can be reduced several degrees by the mere application of stress and their strength in the direction of stress is at the same time increased many fold. Finally, reactions of polymerisation also appear to be uniquely adapted to the chemistry of vital growth because they are the only reactions that are capable of indefinite structural propagation in space.

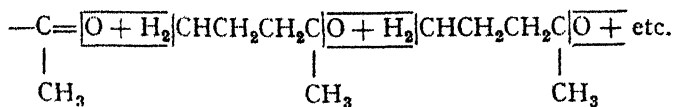
Curious analogies with vital growth are found in granular polymerisations which have as yet received very little published attention, although a few observations on chloroprene in this connection have already been described.⁶

If we place a few grams of liquid chloroprene in the bottom of a long tube together with a little catechol to inhibit polymerisation, chill the tube, pump it out thoroughly and seal the top at the lamp, the tube may be allowed to stand upright for weeks without the appearance of any change. But if we concentrate a strong beam of light on a small spot at the top of the tube, a minute speck of white solid will appear within a short time. The light may then be removed: the speck will grow to a cauliflower-like mass at the expense of the vapours and thence of the liquid monomer until the latter is exhausted. The polymer on superficial inspection seems to be a mass of globules or cellular crystals, but X-ray examination reveals no crystalline pattern. The growth of the mass apparently occurs at different rates in different directions. Sometimes lateral growth is more vigorous than vertical, and the mass will then burst the walls of a very heavy tube, although the total volume of polymer is only a fraction of the available space. Any fragment of the granular mass when placed in fresh chloroprene liquid or vapour will act as seed around which further growth occurs. The viability of the mass as seed will usually persist on standing in laboratory air for several days, but finally it is lost. Similar observations can be made with butadiene and other materials. The analogies of this process with vital growth are obvious. The process may be labelled heterogeneous autocatalysis, but the mechanism of the catalytic effect is obscure. Reactive centres in the sense of free radicals are scarcely admissible, since the viability persists in air, and for various reasons neither adsorption nor solution seems to offer an adequate explanation.

Many different types of synthetic polymers can be made, but no naturally occurring polymerisation has yet been exactly simulated. Why should we not be able to synthesize cellulose, or proteins, or rubber? We can make innumerable members of each of these types: polyacetals, polyamides, and polyprenes. We can even make polyprenes that equal natural rubber in strength and elastic extensibility and are superior to it in many other respects, but the method (*i.e.*, the polymerisation of chloroprene) is as yet subject only to empirical methods of control and not to rational methods based on completely elucidated theoretical principles. Besides, this goal has not yet been approached starting from isoprene, and it is not at all certain that nature builds up rubber directly from isoprene: she might, for example, start with methyl-*n*-propyl

⁶ Carothers, Williams, Collins and Kirby, *J. Am. Chem. Soc.*, 1931, **53**, 4214.

ketone and carry out a selective condensation polymerisation completely evading the diene intermediate.



The synthesis of proteins raises a different set of questions. α -amino acids (or their esters) can be polymerised directly in vitro, but the product is usually the cyclic dimer (diketopiperazine). But in the organism, cyclisation apparently does not occur: reaction is exclusively intermolecular and a linear polyamide results. Generally speaking, cyclisation and chain formation represent two paths, the choice between which is determined almost completely by the nature of the initial reactant (especially its unit length).⁷

The conditions in vitro presumably are the normal ones of chance. If both reactions follow the same mechanism, we can say that in a compound of the type $\text{NH}_2\text{CH}_2\text{CONHCH}_2\text{COOH}$, intramolecular approach of the terminal groups is more frequent than intermolecular (which means cyclisation in vitro), but in the organism the probabilities are reversed and chain formation occurs. How can this be? Temperature and moderate dilution have small control over such matters, and perhaps then in the wrong direction. But if reaction is preceded by adsorption at an interface, as it might be biologically, the molecule is no longer free to assume its spatially probable configuration. Its head, tail, and middle are fastened to a surface and the only terminal approaches then possible may be intermolecular. This picture is not here proposed as a solution of the mechanism of protein synthesis: it is introduced rather as an interestingly conceivable possibility, but especially for the purpose of emphasising the following points: ring formation and chain formation are the two alternatively possible results of every bifunctional reaction; complete control over these alternatives is possible only by bringing the ends of the molecules together or separating them at will; the only apparent prospect of achieving this result lies in the use of surface forces; reactions in vivo probably occur largely at surfaces; and in any event the effect of surfaces on bifunctional reactions presents an almost completely unexplored field (except for the interesting preliminary work of Freundlich and of Salomon).⁸

3. Polyfunctionality.

Polymerisations generally may be divided into those that are bifunctional and those of higher orders. We may take an hydroxy acid as an example of the bifunctional type:



The two reacting molecules are monomers; the first product is a dimer, since it contains two structural units. At this point, half of the initial functional groups have disappeared; similarly, it is evident that the formation of two ester linkages (trimer) will involve 67 per cent. reaction, a tetramer will correspond with 75 per cent. reaction, etc. In general, if

⁷ Carothers, *J. Am. Chem. Soc.*, 1920, **51**, 2548; Hill and Carothers, *ibid.*, 1933, **55**, 5023.

⁸ *Helv. Chim. Acta*, 1934, **17**, 88.

p is the degree (fraction) of reaction and \bar{x} is the average degree of polymerisation,

$$(1) \quad p = 1 - \frac{1}{\bar{x}}.$$

The following values are further illustrative :—

p	0	0.5	0.8	0.9	0.95	0.99	0.999
\bar{x}	1	2	5	10	20	100	1000

The average molecular weight rises very steeply with increasing degree of reaction beyond 0.95, and hence it is not impossible (as some authors maintain) to obtain very large molecules from condensation polymerisations. If p should reach one the molecular weight would become infinite.

As a hypothetical example of a more highly polyfunctional reaction, we may take an acid $R(\text{COOH})_4$ and consider the result of intermolecular anhydride formation. We assume that the structure and conditions are such that no intramolecular reaction occurs at any stage. Representing the acid by A^4 the anhydride would be



etc., where the superscripts indicate that each unit bears two unreacted carboxyls. Hence when all of the molecules have been combined into one (and no further intermolecular reaction therefore can occur) only 50 per cent. of the initially present functional groups have disappeared, *i.e.*, $p = 0.5$. The formation of branching chains of course does not affect this conclusion.

A general equation relating degree of reaction, polymerisation, and functionality can be developed.

Let f = degree of functionality (*i.e.*, number of functional groups per monomer molecule).

N_0 = number of monomer molecules initially present.

Then $N_0 \cdot f$ = number of functions initially present.

N = number of molecules after reaction has occurred.

$2(N_0 - N)$ = number of functions lost.

$\frac{2(N_0 - N)}{N_0 \cdot f}$ = fraction of functions lost = p = extent of reaction.

Obviously, $\frac{N_0}{N} = \text{average degree of polymerisation} = \bar{x}$.

Hence

$$(2) \quad \frac{2}{f} - \frac{2}{\bar{x} \cdot f} = p = \text{degree of reaction}.$$

This equation has interesting applications. If we heat together a dibasic acid and a glycol, a linear polyester is formed. As the reaction, measured by the disappearance of acid progresses, the average molecular weight rises, presumably in accordance with equation (2). Reaction becomes exceedingly slow after it is 99 per cent. complete, and the calculated molecular weight approaches 15,000 to 20,000. But no matter how far the reaction is carried under normal conditions, the product is both fusible and soluble.

If in a similar manner a dibasic acid is heated with glycerol, one observes at first that the viscosity of the mixture changes only slowly as reaction proceeds, and then it rises to infinity while much of the acid

remains still unreacted. The product is completely infusible and insoluble.

Obviously, bifunctional reactions can yield only linear polymers; and there is evidence among such polymers that solubility and fusibility are not lost even at very high molecular weights. But reactions of higher orders always present the possibility of spreading out in three dimensions.

Returning to the anhydride symbolised above as

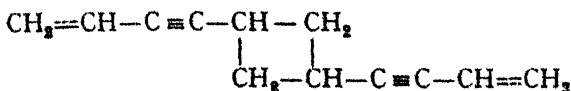


let us suppose that the chain is 100 units long, and bears 200 carboxyl groups. Such a molecule could easily be soluble and fusible. If further intermolecular reaction occurs, the chain must become cross-linked. Obviously, when 2 carboxyls have been lost from each chain, all the chains will be locked into a single molecule. This involves the loss of 1 per cent. of the remaining carboxyls: and it will certainly be accompanied by the disappearance of fusibility and solubility: a gram of matter cannot exhibit the kinetic behaviour of a single molecule.

Referring again to formula (2) if x is very large the second term disappears, and we have $p = 2/f$ which tells at what degree of reaction the molecular weight will become infinite, or where, in polyfunctional reactions, gelation will occur and intermolecular reaction cease.

For a bifunctional reaction $p = \frac{2}{f} = 1$, and since this value never can actually be reached, gelation will not occur. For a trifunctional reaction, the limit will lie at $p = \frac{2}{3}$, for a tetrafunctional reaction at $\frac{1}{2}$. We may note in passing that for this reaction at $x = 100$, $p = 49.5$ per cent.; thus the average molecular weight will suddenly change from a moderate to a colossal value with very little change in the extent of reaction: and so far as the utility of the formula is concerned, it is not important whether the transition in properties occurs at a molecular weight of 10^5 or 10^{20} .

In attempting to apply formula (2) the chemistry of the situation must, of course, be taken into account. A double bond will count as a double function only if reaction is exclusively intermolecular at every stage. Multiple function compounds often do not exercise all their functions together. In the formation of polyprenes from dienes, only the 1, 4-positions of the latter are at first called into play. The remaining double bond of each unit functions under slightly different conditions to cause cross-linking. Acetylene would be a tetra-functional compound and probably behaves as such in the formation of cuprene. In the formation of divinyl acetylene,⁹ $\text{CH}_2=\text{CH}-\text{C}\equiv\text{C}-\text{CH}=\text{CH}_2$, only half of its unsaturation is involved. This material again in the early stages of its thermal polymerisation behaves like a bifunctional compound yielding, for example,¹⁰



but gelation usually occurs long before all of the divinyl acetylene has reacted.

⁹ Nieuwland, Calcott, Downing and Carter, *J. Am. Chem. Soc.*, 1931, **53**, 4197.

¹⁰ Cupery and Carothers, *J. Am. Chem. Soc.*, 1934, **56**, 1167.

Perhaps a majority of the reactions to which equation (2) would be applied are of the A—B type involving two reactants of complementary function. It is evident that if each reactant is bifunctional, A^2B^2 , the reaction as a whole will be in effect bifunctional: A^3B^3 is trifunctional, etc. But if A and B have a different number of equivalents per molecule, the situation is more complicated. We can distinguish two different possibilities:

(a) Suppose that on the average every coupled molecule of A involves also the coupling of an equivalent number of molecules of B; then the degree of functionality is the average number of functions per molecule of the two reactants when they are taken in equivalent amount. Thus in the reaction of glycerol and phthalic anhydride (A^3B^2) we have to take 2 moles of glycerol and 3 of the acid, or 5 altogether, containing 12 equivalents and $f = \frac{12}{5} = 2.4$. Then at $x = \infty$, $p = \frac{2}{2.4}$ and the limit of the reaction will be $\frac{2}{3}$ (83.3 per cent.). This, in fact, represents the *maximum* amount of reaction that can occur before gelation under any distribution of combinations, provided only, of course, that the reaction is all intermolecular.¹¹

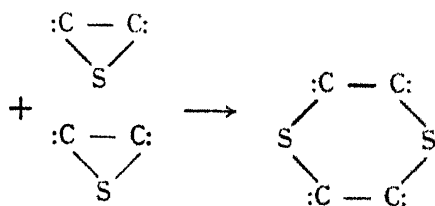
(b) Another extreme possibility is the following: Suppose the glycerol behaves at first as though it were bifunctional yielding a chain



(' indicates unreacted hydroxyl). Then all of the molecules of glycerol could be combined into one with the loss of only $\frac{2}{3}$ of the functional groups (of course $\frac{1}{3}$ of the phthalic anhydride remains entirely unreacted). Here $f = 3$ and 66.7 per cent. is the minimum extent of reaction compatible with gelation. Experimental values found by various investigators for the extent of reaction at gelation generally lie between 75 and 80 per cent.¹²

Reactions of polymerisation involving degrees of functionality running into the hundreds or thousands are undoubtedly of great importance. The vulcanisation of rubber is an example. The preponderance of evidence lies in favour of the view that vulcanisation is the result of cross-linking through reaction at the double bonds. A conservative estimate of the number of double bonds in the average rubber molecule is 5000. Suppose the mechanism of vulcanisation is as follows: At some double bond $:C=C: + S \longrightarrow :C-C:$. Sulphides of this struc-

ture are known to be unstable, and further reaction might occur with a similar group in a neighbouring molecule,



¹¹ A similar calculation for the glyptal reaction has already been made by Bozza, *Giorn. chim. ind. applicata*, 1932, 14, 400.

¹² Bozza, *loc. cit.*¹¹; Kienle and Hovey, *J. Am. Chem. Soc.*, 1929, 51, 509.

At a minimum then all the rubber molecules could be locked together when only 0.04 per cent. of the double bonds had disappeared, or about 0.02 per cent. by weight of sulphur had reacted. A good estimate for a probable maximum is difficult to make. Experimentally, the minimum amount of sulphur required for the beginning of vulcanisation¹³ is about 0.15 per cent. Staudinger and Heuer have shown¹⁴ that as little as 0.01 per cent. of divinyl benzene in styrene will lead to the formation of an insoluble polymer.

4. Molecular Weights and Molecular Weight Distributions.

The peculiarities of high polymers are due to the fact that their molecules are very large. Estimates of molecular weights are therefore of the utmost importance, but they are very difficult to obtain. Direct osmotic methods present great practical difficulties. Staudinger has proposed to infer molecular weights from the viscosities of polymer solutions. There appears to be no doubt that, other things being equal, the viscosity of such solutions will increase with increasing molecular weight, and viscosity methods are unquestionably of great value as a means of providing rough estimates concerning the relative order of magnitude of molecular weights in a given polymeric series. But the absolute values inferred from viscosities are subject to a very large factor of uncertainty. An initial difficulty lies in the fact that no generally valid relation between viscosity and concentration in solutions of linear polymers has yet been established. Presumably some simple and general relation will be found to exist in solutions that are sufficiently dilute but possibly only at dilutions requiring a higher degree of experimental precision than is now generally available. (In theory, of course, extrapolation to infinite dilution is always possible, but practically such extrapolations may also involve large uncertainties.)

Aside from this point, there is one theoretical complication that has as yet received relatively little attention. High polymers are generally mixtures covering a wide range of molecular species. The properties of a polymeric mixture will depend not only upon the average molecular weight, but on the manner in which the different molecular species are distributed about the average. Moreover, as Kraemer and Lansing¹⁵ have recently shown, it is possible to define various types of averages :

specifically, for example, there are the number average $M_n = 1/\sum \frac{f_i}{M_i}$, and the weight average $M_w = \sum f_i M_i$, where f_i is the fractional weight of the constituent of molecular weight M_i in the mixture, and the summation is applied to all the constituents. The number average is the conventional one: it is this that is inferred from osmotic methods or chemical measurements of end groups. But all the proposed viscosity relations would give M_w .

If a material is homogeneous, M_n and M_w will be identical: but if we are dealing with a mixture they will generally be different. If we have 10 molecules of weight 100 and 5 of 1000, M_n is 400 but M_w is 851. Thus a correlating factor for molecular weight vs. viscosity arrived at by

¹³ Bruni, *Rev. gen. Caoutchouc*, 1931, 8, No. 75, 19; Stevens and Stevens, *J. Soc. Chem. Ind.*, 1932, 51, 44T.

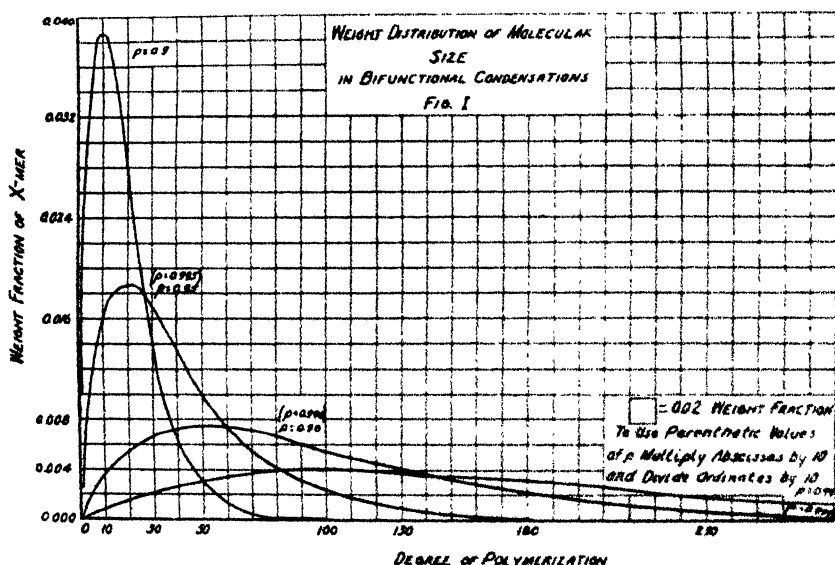
¹⁴ *Rev.*, 1934, 67, 1164. See also *ibid.*, 1935, 68, 1618.

¹⁵ *J. Physic. Chem.*, 1935, 39, 165; *J. Am. Chem. Soc.*, 1935, 57, 1369. See also Kern, *Rev.*, 1935, 68, 1439, and Staudinger, *Helv. Chim. Acta*, 1929, 12, 941.

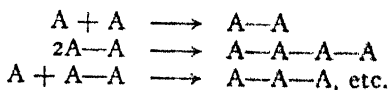
observations on a homogeneous material is almost certain to give erroneous values when applied to a polymer. And unless the type (distribution) of heterogeneity in all polymers is nearly the same, there cannot possibly be any exact generally applicable correlation between viscosity and molecular weight.

As Kraemer and Lansing have pointed out, the Svedberg ultracentrifuge provides the only means yet available for determining experimentally both the average molecular weight and the distribution in polymeric mixtures. But this method is not simple, and the apparatus is very costly, and hence experimental data are as yet extremely meagre.

It is therefore a matter of considerable interest to make calculations as to the theoretically probable distribution of molecular species in polymerisation reactions. Such calculations have been made by Dr. P. J. Flory¹⁶ of this Laboratory, and it may be worth while to give a brief indication of some of the results.



The simplest case is the formation of a linear condensation polymer. Here we have a series of stepwise reactions



always involving the same functional groups. Whatever may be the general effect of viscosity on reaction rate, the inherent relative reactivity of a functional group will presumably be but little affected by the length of the molecule to which it is attached. If this assumption is correct, it is possible to show that

$$\Pi_x = xp^{x-1}(1-p)^2,$$

where p is the extent of reaction and Π_x is the fraction of units present in x -mers (which also equals very nearly, except for low values of p , the weight fraction of x -mer).

In Fig. 1, Π_x is plotted against x for various values of p . It is evident

¹⁶ Unpublished results.

that we are dealing with a wide distribution of species. Certain relations are most briefly shown by means of an example.

If we assume that the weight of the mer or unit is 100, and reaction has been carried to 98 per cent. of completion ($p = 0.98$), then M_n , the number average molecular weight is 5000, and the maximum in the distribution curve also occurs at this point. But the nature of the curve is such that only 26 per cent. by weight of the material has a molecular weight below 5000, while 74 per cent. has a weight at or above 5000. Moreover, 40 per cent. of the material has a molecular weight above 10,000. Finally, the weight average molecular weight is 9900 or nearly twice the number average.

Mechanical properties, such as toughness and tensile strength, certainly require the presence of very large molecules. But it is not at all certain that these properties will be improved by the elimination from a material of all fractions having low or moderately high molecular weights. In rubber and cellulose plastics the deliberate addition of small foreign molecules (plasticisers, lubricants, etc.) often has a very favourable effect on properties. It is probable that average molecular weights *per se* will furnish an entirely inadequate basis for the interpretation of those properties which are chiefly of interest in dealing with high polymers. The study of molecular weight distributions and their relation to properties thus presents a field which should ultimately be of great importance to the subject of polymerisation.

GENERAL DISCUSSION

Professor R. Signer (Bern) said: Carothers concludes that, in order to establish the properties of a highly polymerised substance, we must take into account not only the mean molecular dimension but also the molecular weight distribution. He suggests that polydispersity may chiefly be established by the use of the Svedberg ultra-centrifuge, but adds that it is essential that the experimental data are as yet extremely meagre. In this connection we observe that recently¹⁷ R. Signer and H. Gross in Svedberg's laboratory conducted extensive experiments on the molecular weight distribution of polystyrenes. It appears that determinations of polydispersity by measurement of sedimentation velocity can only be effected in extremely dilute solutions. At large concentrations the fibre molecules are entangled or matted, so that, whether short or long, they move with equal velocity. It is also essential to use very intense centrifugal fields; the sedimentation process must be carried out so rapidly that the diffusion of the fibre molecules can be neglected. With Svedberg's apparatus both these conditions may readily be fulfilled.

Dr. R. Houwink (Eindhoven) said: Formula (2) is only applicable to bifunctional reactions. It seems very questionable whether it can be applied to polyfunctional reactions, as will be seen from Fig. 1. As soon as the two polymers, A and B, have reacted at the spots 1 and 4, each further reaction, *e.g.*, between spots 2 and 5, or between spots 3 and 6,

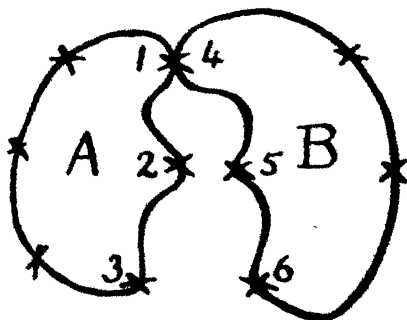


FIG. 1.—The functional groups are indicated by x.

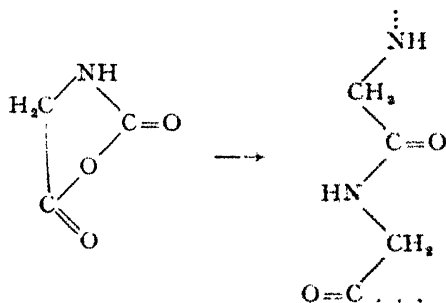
¹⁷ *Helv. Chim. Acta*, 1934, 17, 726.

will result in a further decrease of the number of functions, *whereas no change in N or N_0 takes place*. It does not therefore seem justified to say in such a case that the number of functions lost is $2(N_0 - N)$. Since formula (2) has been developed on such a basis, however, that formula cannot be right.

Dr. H. B. Weiser (*Houston, Texas*) said: If the term molecular weights is to continue to have any real significance, it should be restricted to its time-honoured use. In the colloidal systems under consideration to-day, the particles are in many cases aggregates of polymerised molecules, and not individual polymerised molecules. If the size-distribution in such systems is more or less uniform, determinations may be made of the so-called "molecular weights" by sedimentation methods. But in the case of aggregates it is the "particle weights" and not the molecular weights which is obtained by such methods. Using Zsigmondy's nuclear procedure, a large number of samples of colloidal gold may be prepared in varying particle size from extremely minute to relatively large. But in each sample the particle size is approximately uniform. Gold, therefore, may be made to have any "particle weights" one pleases within rather wide limits. It seems absurd to say that gold has any number of molecular weights. Irrespective of whether we are dealing with relatively simple inorganic systems or with highly polymersed organic systems, it is suggested that the term "molecular weights" be applied only in its original sense when the evidence indicates that we are working with the individual molecules; and that the term "particle weight" be used *in cases of doubts*, or where the particles are known to consist of aggregates of molecules.

Professor K. H. Meyer (*Genève*) said: Dr. Carothers has spoken of the polymerisation of amino-acids, which *in vitro* give the cyclic dimer, and *in vivo* build up the long protein chains. He spoke of the possibility of polymerisation *in vivo* taking place on interfaces and being influenced and directed by fields of force in the cellular interfaces. I do not think that one ought to attribute this effect to the interfacial forces, which seem to be greatly over estimated by biologists. The interfacial forces in the organism must be somewhat small, owing to the presence of so many substances with interfacial activity, which lower the tension at the interfaces and reduce the interfacial forces. The forces in the cell interfaces cannot be compared with the forces at a carbon surface, but at the most with the forces in an oil-water interface.

It seems safe to assume that the organism uses indirect chemical ways to guide reactions. It may be of interest, that a derivative of amino-acids, the cyclic anhydride discovered by Leuchs,¹⁸



is readily transformed into polypeptides of very high molecular weight, with liberation of carbon dioxide.¹⁹ We think that the organism may form the long chains by similar means.

¹⁸ *Ber.*, 1906, **39**, 857; 1908, **41**, 1721.

¹⁹ K. H. Meyer and J. Go, *Helv. Chim. acta*, 1934, **17**, 1488.

Professor H. Mark (*Wien*) said: Dr. Carothers' results, especially those in Fig. 1, where one finds the distribution of chainlength at different stages of reaction, are most interesting. The formula which leads to this figure is derived under certain suppositions. First, it was assumed that the chain may be built not only by addition of the saturated monomeric molecule, but also by mutual additions of chains, which have already reached a certain length. In fact, it is very likely that both kinds of reaction take place; but it seems rather improbable that the rates of these two reactions are also equal.

In any event, knowledge of the chain distribution at a given stage of polymerisation is of the greatest interest for the mechanism of reactions of this kind, and it is very important to have as many methods as possible to work out such a distribution curve experimentally. So far, this has only been accomplished in the well-known work of Signer on polystyrene by means of Svedberg's ultracentrifuge. Dr. Carothers has a very extensive experience in dealing with high molecular substances; does he know any other reliable method, whereby one could work out a distribution curve of the type shown in Fig. 1. This seems to be especially important, because the ultracentrifuge is a very expensive and complicated apparatus, which only exists in two different places in the world.

I would like to add, that there is some possibility of estimating the distribution of chains, if one takes in account the different average types in determining the molecular weight of high molecular substances from the viscosity and from the osmotic pressure; these Carothers calls "number average" M_n and "weight average" M_w . When the two methods lead to different results, there must be a rather remarkable difference in the length of the chains, contained in the sample.

Professor H. Staudinger (*Freiburg i. Br.*) said: Among the high molecular organic compounds, *i.e.*, the compounds which are built up of macromolecules, high polymers are of particular importance. Having regard especially to the different new experimental procedures in this field it is necessary to discuss the question of the nomenclature of these substances.

All high molecular weight products consist of macromolecules of such size that the physical and chemical properties of molecules of approximately equal structure and equal size differ so little that a mixture of these cannot be separated into their components. The high polymeric materials consist of *macromolecules* which represent a mixture of *polymeric homologous compounds*, *i.e.*, a mixture of macromolecules which differ only in the degree of polymerisation. Hence, high polymeric materials are built up from one and the same basic molecule ("*Grundmolekül*") in such a way that numerous basic molecules are combined by primary valency bonds to form the macromolecules. In the case of heteropolymers, not only one but several different basic molecules participate in the building up of the high polymeric macromolecule. The mixed polymers of styrene and maleic anhydride, *etc.*, are heteropolymers.²⁰ Furthermore, the polyesters may be considered as heteropolymers, since in their macromolecules several basic units are combined in the same way. Thus, the polyesters obtained from succinic acid and glycol are built up of succinic anhydride and ethylene oxide. The above polymers, with the exception of molecules which are rings of high molecular weight are, strictly speaking, not real high polymers, since the end groups of such molecules are built up in a different manner from the chain, in which the atomic arrangement of the basic unit is repeated regularly.²¹

High polymeric materials can be formed in different ways. First, they

²⁰ Wagner-Zauregg, *Ber.*, 1930, **63**, 3213.

²¹ In this case also it is possible that the arrangement of the basic molecules in the chain is not regular, as is observed with polyoxymethylene. (Compare *Liebigs Annalen*, 1929, **474**, 232).

can arise by polymerisation of unsaturated compounds. In this case, as has been pointed out in contribution No. 6,²² one can discriminate between *true polymerisation processes* and *condensation polymerisation processes*. In true polymerisations the polymeric molecules possess the same atomic arrangement as is present in the basic molecule. In the condensation polymerisations, on the other hand, a shifting of atoms, e.g., hydrogen atoms, takes place. High polymeric products can also arise from low molecular ring systems. Ethylene oxide can be transformed into polyethylene oxide, lactones into polyesters. Finally, the formation of high polymeric products can also take place by a *polycondensation* process in which numerous reactive molecules condense. Thus, the polyesters are formed from the esters of hydroxy acids by intermolecular esterification of numerous single molecules through loss of water, i.e., by a process which cannot be designated as a polymerisation process, if one maintains for the latter the old definition. Following this definition, a *polymerisation process* is a process in which a substance of low molecular weight is transformed into a substance of equal composition but of higher multiple molecular weight. Hence, polyesters should best be designated as *polycondensation products*, if one wishes to characterise their manner of formation.

These questions of nomenclature may be further illustrated in the case of cellulose. This high molecular substance may be designated as "high polymeric," since the cellulose molecule is built up of numerous similar basic molecules of glucose anhydride. However, if one wishes to emphasise the building up of cellulose from glucose or cellobiose, then cellulose is a polycondensation product of these saccharides. In the case of many high molecular substances there are special reasons which decide whether they ought to be considered as polymerisation or polycondensation products. The phenol formaldehyde resins, e.g., "bakelite," can be designated as polycondensation products, since it is not certain that one and the same structural unit occurs regularly in the three-dimensional macromolecules of the resin.

Dr. R. Houwink (Eindhoven) said: Is it the intention of Dr. Carothers to distinguish in future between "polymerisations" and "condensations" as heretofore? Will the new definition of "condensations" then be: intermolecular combinations which are functionally capable of proceeding indefinitely with the elimination of elements or simple compounds?

Dr. W. H. Carothers (Wilmington), said, in reply to Dr. Houwink: The application of formula 2 to the calculation of molecular size naturally involves uncertainty, since it depends upon the arbitrary assumption that reaction is *exclusively* inter-molecular. This condition surely is not exactly fulfilled, especially in highly polyfunctional reactions where the calculated molecular weight is rapidly approaching infinity. The approximate validity of this assumption has, however, been demonstrated experimentally in appropriate simple cases, and its use for illustrative purposes seems to be well justified.

In reply to Dr. Weiser: The question of the relation between molecular weight and particle size is, I think, in many cases not capable of any simple solution, but for the simpler types of organic polymers it is possible to assign a definite and rather exact significance to the term molecule (as Professor Staudinger has done) and to demonstrate by chemical means that the chemical molecule is the osmotic particle under consideration.

In reply to Dr. Meyer: The N-carboxy-anhydrides of the α -amino-acids discovered by Leuchs are indeed compounds of great interest. Attention has already been drawn to the possibility that they may constitute intermediates in the protein synthesis. From this standpoint they are compounds that certainly deserve a great deal more study.

In reply to Dr. Mark: Unfortunately, I am not aware of any chemical method for determining molecular weight distributions. Apparently the

²² Compare also H. Staudinger, *Ber.*, 1920, **53**, 1081.

only method yet available is that of the ultra-centrifuge, which, in connection with lyophilic polymers, has lately been used for this purpose by Lansing and Kraemer and by Signer.

Professor Staudinger's point of view has considerable historical justification, but it presents certain logical and practical difficulties. Apparently it involves the necessity of making a distinction between polymers and "real polymers" and of admitting that polymers can be formed by reactions that are not polymerisation.

The essential point of the conventional definition is that a monomer and its polymer have exactly the same composition. But this condition is not in fact satisfied in many of the cases to which the name polymer has become firmly attached. Professor Staudinger was himself the first clearly to recognise this in the case of the polyoxymethylenes. Nevertheless he still refers to them as polymers and only occasionally adds that they are not so, strictly speaking. The determination of composition with sufficient precision to demonstrate the absence of foreign terminal groups in very long molecules is experimentally very difficult. It is possible that among such materials no "polymers strictly speaking," exist. But it is one of the aims of scientific terminology to permit one always to speak strictly, and this becomes impossible if definitions are formulated to include conditions that are not open to experimental test.

As a matter of actual fact, chemists use the terms polymerisation and polymer without pretending to wait for evidence that reactions consist in pure self-addition, or that the condition of identical composition is satisfied. Thus, by implication it seems to be recognised generally that the characteristic and peculiar feature of polymerisations resides in something not compatible with the conventional definitions. The statements offered in the first section of the above paper constitute an attempt to indicate what is this characteristic and peculiar feature.

In connection with Dr. Rideal's interesting survey of the general field, I should like to raise one point. The term "linear polymer" was, I believe, first introduced in 1929. It was explicitly intended to include both open and closed chains. The necessity for this arises from the fact that the terminal groups may, in many cases be undetectable, even when they are present, and it is unwise to include in a definition any conditions that are not subject to experimental test.

It is true that large molecules are in some cases built up from small ones by reactions that appear, at least, to consist in pure addition, while in other cases they are formed by reactions that are demonstrably condensations. Staudinger proposes to call the latter type of reaction polycondensation (as Chalmers has also). This seems an appropriate term (perhaps it is better than condensation polymerisation which Staudinger prefers to use for another purpose), but I contend that we may as well give in to the logic of the situation and admit that such reactions constitute one type of polymerisation: the products are polymers (Staudinger himself calls them such in his remarks above). Besides they can in many cases be smoothly depolymerised to the corresponding cyclic monomers, and reversal of this process then yields a product which is often indistinguishable from the original polycondensation product. (These last remarks are also offered in reply to Dr. Houwink's second question.)

THE MECHANISM OF POLYMERISATION.

BY H. DOSTAL AND H. MARK (Wien).

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A certain number of polymerisation-processes—especially some organic reactions of this kind—were thoroughly investigated many years ago.¹ They owed this early interest to the fact that the products which they yield have some unusual properties, interesting from the point of view of pure science—and sometimes from that of industry as well. For a long time uncertainty prevailed about the kind of molecules of which these substances are composed, ordinary methods of molecular weight determination failing to give an answer to this question.² The insolubility and extremely low vapour-pressure of the polymeric substances make it impossible to determine their molecular weight in the gas-phase or in the state of dilute solution, and the size of their molecules can only be estimated by other, less reliable methods.³ In the course of years, however, a conception arose, which presumed the substances in question to be built up of long chain-molecules. The exact length of the chains is supposed to depend on special conditions of polymerisation, but to be generally very great as compared with that of ordinary molecules. Methods have been devised for the determination—at least approximately—of the molecular weight of such chain-molecules. The first qualitative investigations of the polymerisation-reactions are due to Anschütz, Auwers, Harries, Ostromysslensky, Willstätter and others.⁴ Latterly, this field has been systematically investigated by H. Staudinger and W. Carothers. In his well-known monograph *Über die hochmolekularen Verbindungen*, Staudinger⁵ collected a vast amount of material concerning the preparation and properties of these substances. Together with other investigators, he showed convincingly that polymerisations really yield products with long chain-molecules and a molecular weight up to many thousands. Analogous results have been obtained by Carothers,⁷ R. O. Herzog, K. Freudenberg, K. H. Meyer, H. Mark, and others, so that the chain-structure of the polymerisation products can now be considered as a fairly well-established fact.⁶ The experiments showed, however, that polymerisation-products are not chemically pure substances; in the sense that all their molecules are not exactly

¹ For instance, von Anschütz, Auwers, Ostromysslensky, Perkin, and others.

² Compare, for instance, the discussions at the *Naturforscherversammlung*, Düsseldorf, 1926; *Ber.*, 1926, 56.

³ See H. Mark, *Chemie und Physik der Cellulose*, Springer, 1932.

⁴ See, for instance, *Liebigs Annalen*, 1891, 273, 101; *Ber.*, 1891, 24, 1935; 1902, 35, 1186; 1905, 38, 1979.

⁵ Summarised in the fundamental work: *Die hochmolekularen Verbindungen*, Berlin, 1932, Springer.

⁶ See K. Freudenberg, *Cellulose und Lignin*, Springer, 1933; K. H. Meyer and H. Mark, *Hochmolekulare Verbindungen*, Leipzig, 1931.

⁷ For instance, *J. Amer. Chem. Soc.*, 1929, 51, 2548; 1930, 52, 4110; 1932, 54, 314, 711, 4071, 4110, 5023.

⁸ A different view is held by K. Hess, *Lehrbuch der Cellulosechemie*, 1928.

identical. The chains are all built up on the same principle, but with a different actual number of chain-links. Besides polymers of this kind, some polymerisations give products with properties indicating a two-dimensional net-structure or a three-dimensional lattice rather than one-dimensional chains. Probably, in these cases, the chains which are at first formed are linked together in two or three dimensions by valency-forces. So far, however, it has not been possible to state definitely the mean size (or the distribution of sizes) of the molecules in such more complicated cases of polymerisation—as was found to be possible in the simpler case of "one-dimensional" structures.

Considering the great amount of experimental evidence which has been collected in the endeavour to elucidate the nature and properties of the long chain-molecules, we think it timely to discuss more in detail the mechanism of the reactions by which chain-molecules are formed.⁹

In this paper, we shall first give a short summary of the work already done in this direction and then try to bring forward some points of view of our own. The object of our discussion will be the *polymerisation* of unsaturated organic molecules (with double or triple bonds)—*i.e.* of molecules which are able to form chains by simple addition. We will thus postpone to a later occasion the discussion of so-called *condensations*, —*i.e.* reactions in which the original molecules are saturated and lose a constituent part (for instance, H_2O , NH_3 , etc.) in order to form a chain.

1. Experimental Results.

Whereas preparative investigations of the polymerisation-reactions have been very numerous, only few of them contain any observations concerning the kinetics of the polymerisation-process at all. As far as data of this kind can be found, they usually refer to a single preparation and are not a result of a systematic kinetic investigation.¹⁰ This lack of experimental material is probably due to the fact, that measurements of the velocity of polymerisation are by no means simple and require special precautions. It is, in fact, well known that the velocity of many reactions of this kind is strongly diminished by the presence of minute traces of certain foreign substances. We shall show later that these substances act as "anticatalysts." The industry is well aware of this effect and uses substances of this kind as "stabilisers" for certain technical products. The stabilisers probably reduce the velocity of polymerisation by breaking reaction-chains. On the other hand, substances are known, which enormously accelerate the velocity of polymerisations, even when present in a very small concentration. Such is, for instance, the action of sodium on butadiene, of oxygen on β chlorobutadiene, and of iodine on vinyl ether. These "positive" catalysts probably favour the formation of "nuclei," which are starting-points of further polymerisation. The occurrence of positive and of negative catalysis can in fact be considered as a typical feature of polymerisation reactions. This fact provides some useful hints towards the understanding of the mechanism of the reactions in question; but, on the other hand, it makes exact experimental treatment of the problem rather difficult.

Table I. gives a summary of the most important data concerning the

⁹ Compare W. Chalmers, *Canad. J. Res.*, 1932, 7, 113.

¹⁰ For instance, Staudinger and Suter, Whitby and Crozier, Whitby and Katz, and others.

velocity of thermal polymerisation reactions. One sees how scarce is the material available in the literature of the subject. Seldom has the reaction velocity been studied over sufficiently long time-intervals and at different temperatures. Most of the investigations have been carried through with polymerising substances in the pure liquid state, whereas investigations of more or less dilute solutions would give results much easier to interpret. If the best experimental results available are plotted in the form of graphs, reaction-curves of the type shown in Figs. 5 to 8 (p. 17) are obtained. W. Chalmers¹¹ suggested that polymerisation reactions are "quasi-monomolecular," column 5 of Table I. shows that this conception is not without foundation.

TABLE I.

Substance.	Temperature °C.	Time.	Per Cent. Polymerisa- tion.	$K \times 0.4343$.
Styrene (Lautensch- läger)	80°	10 hours	10	1.27×10^{-4}
	—	15 "	18	1.60 "
	—	20 "	24	1.65 "
	—	25 "	26	1.45 "
Styrene (Iorde)	80°	3 hours	0	—
	—	6 "	1.8	—
	—	9 "	7.0	—
	—	12 "	5.5	—
	—	15 "	8.6	—
	—	18 "	11.2	—
	—	21 "	17.4	—
Styrene (Suter)	—	24 "	20.0	—
	130°	1 hour	21	2.85×10^{-3}
Indene (Whitby and Katz)	—	3 hours	45	2.40 "
	140°	25 days	15.9	3.49×10^{-8}
	—	70 "	45.35	4.34 "
	178°	1 day	5.02	2.59×10^{-7}
	—	2 days	12.4	—
	—	3 "	18.55	—
	—	4 "	26.3	—
	—	11 "	65.5	4.86×10^{-7}
	—	16 "	70.6	—
	—	19 "	74.15	—
	—	30 "	82.2	2.89×10^{-7}
	200°	1 day	22.7	1.29×10^{-6}
	—	2 days	38.7	—
	—	3 "	49.1	1.13×10^{-6}
	—	4 "	70.3	1.81×10^{-6}
	—	8 "	89.3	—

True, the velocity-constants, calculated as for a monomolecular reaction, show variations up to 50 per cent. of their mean value; but—in some cases at least—there is no definite trend, and the irregular variations may therefore be ascribed to experimental errors. However, a more detailed analysis of the reaction-mechanism leads us to a much more complicated kinetic law. Our task will be to test this law by comparing its predictions with experimental results.

¹¹ Compare also W. Chalmers, *J. Amer. Chem. Soc.*, 1934, 56, 917.

Recently, systematic investigations of the polymerisation of styrene and of acryl ester at different temperatures have been started with pure liquids as well as with solutions. Some results of these experiments are given in Figs. 5 and 5a. We recognise a short "induction" period, followed by a long interval in which the polymerisation-velocity remains constant. Finally, as the polymerisation is nearly completed the reaction velocity slows down, and the system approaches asymptotically the limiting state of complete polymerisation.

This behaviour is especially clear in the case of styrene, which has been thoroughly investigated by Raff and Iorde. These experiments form the foundation of our further theoretical discussions. We intend to show that satisfactory accordance between theory and experiment can be obtained on the assumption that the polymerisation is a two-stage process.¹² The first stage is the formation of "nuclei," for instance, by collisions between two monomeric molecules. This stage requires an activation, which can be a thermal, photochemical or catalytic one; it can occur mono- or bi-molecularly. In the next section of this paper, formulae will be developed for all these special cases.

In the cases of thermal polymerisation of the ethylene derivatives, especially of styrene, of the vinyl esters and vinyl chlorides, of the acryl esters, etc., experiments indicate a thermal, bimolecular mechanism of the formation of nuclei. When two styrene molecules meet with sufficiently high energy, the two double bonds are "opened" and doubly unsaturated dimeric radicals can be formed, of one of the following kinds:

either: $\text{---CHX---CH}_2\text{---CHX---CH}_2 \dots$
or: $\text{---CHX---CH}_2\text{---CH}_2\text{---CHX} \dots$

We may consider the formation of a nucleus, in a case such as this, as an ordinary bimolecular process, with a collision-factor of the usual order of magnitude, and an activation-energy of 30-50 cal. per mol. An analogous explanation can be supposed to hold for the polymerisations of other ethylene-derivatives, so long as reactions in the dark and without catalysts are alone concerned.

The cause of the inability of ethylene itself to polymerise must be sought in a higher stability of its double bond, which is loosened by substituents. This assumption accords with the general difference in the chemical properties of ethylene and of its derivatives. The dipole structure of the derivatives may contribute to the acceleration of the reaction by which polymerisation nuclei are formed, because dipole molecules possess stronger van der Waals' attractions and come, therefore, into closer touch during collisions.

In the case of *photochemical* polymerisations (for instance, of acrylic esters, of butadiene, etc.) we can expect nuclei to be formed according to a monomolecular law. The monomeric molecule is activated by absorption of light, so as to be able to form a nucleus when colliding with an ordinary non-active molecule. In the next section, formulae referring to this case will also be given.

Very often polymerisations are caused by *catalysts*, as, for instance, by sodium in the case of butadiene, or by oxygen in that of butadiene-chloride.¹³ Important investigations by Ziegler¹⁴ proved, that sodium

¹² Compare also W. Chalmers.⁹

¹³ Compare e.g., Ziegler and Bahr, *Ber.*, 1928, 61, 254; *Lieb. Ann.*, 1929, 473,

¹⁴ See W. Carothers, *loc. cit.*⁷

and other alkaline metals increase the velocity of formation of polymerisation nuclei by "adsorption" on the double bonds. Oxygen acts in the same way in the polymerisation of chloroprene, as Carothers found in the course of his extensive investigations. Because of the complications which may occur in cases of catalytic polymerisation, we shall at first exclude them from our discussion. It would be relatively easy to introduce catalytic effects into our formulae, if only these effects could be restricted to the velocity of formation of the nuclei.

The formation of nuclei may be considered as the first necessary step of every polymerisation process. Its result is the production of a number of activated molecules or reactive radicals.

There are essentially different ways in which these molecules or radicals may further react.

(1) The nucleus may collide with a second monomeric molecule of the initial substance, combine with it and *grow* in this way. The unsaturated character of the one of the collision partners leads us to expect a somewhat low activation energy for this reaction, and the velocity of chain growth can therefore be high as compared with the velocity of the formation of nuclei. The formulae given below show that the formation of a relatively large number of short chains or of a smaller number of long chains depends on the relation between the velocity of formation of nuclei and that of the chain-growth. If the absolute values and the dependence on temperature of both these velocities are known, the whole process is quantitatively described by our equations—with the exception of some side-reactions which will be discussed later. The results of many investigations—especially by Bonhoeffer, Hinshelwood, and Polanyi¹⁵ showed that the activation-energy of chain-growing reactions is usually of the order of 5 Cal. per mol only, which means a very high reaction-velocity indeed. It is, however, to be remembered that, as soon as the molecules become long enough, the collision-factor cannot be expected to be the same as it was before. The reactivity of the active ends of the chain may be inhibited by other parts of the large molecule. In general, we may expect the "sensitive" region of a chain molecule to become smaller with growing length of the chain, despite the fact that the molecule still bears on its ends the same unsaturated radicals. This effect can be taken into consideration in developing the formulae; but we shall disregard it at first, and consider the velocity of chain growth to be a constant, dependent only on temperature and not on the length of the chains.

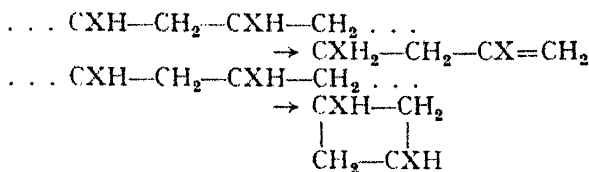
(2) The repeated addition of monomeric molecules is not the only way in which the nuclei may react; there exists a number of other possibilities. The simple picture of the polymerisation process, which was given above (and which has been also discussed before) becomes complicated by these additional possibilities; but only by their full consideration is the theoretical scheme adequate to describe the great variety of the experimental results.

(a) Firstly, let us consider the possibility of a nucleus reacting not with an additional monomeric molecule, but with a second nucleus. The velocity of chain-growth may be further increased and the formation of longer chains favoured by reactions of this kind. That they actually occur may be seen from the kinetics of the condensation reactions

¹⁵ See, for instance, K. F. Bonhoeffer, *Ergeb. exakt. Naturw.*, 1927, 204; Bonhoeffer and Hartack, *Grundlagen der Photochemie*, Steinkopf, Leipzig, 1933, p. 210, where further references are given.

of polybasic acids with polyvalent alcohols. Were it not for the occurrence of reactions of the last-mentioned kind, we could hardly expect the velocity of chain-growth to exceed the velocity of the formation of nuclei in this case too. The whole kinetics of the polymerisation must be therefore different from that discussed above. Experiments show, however, that this is not the case; indeed, condensation reactions of this kind lead to a similar distribution of chain lengths as the ordinary polymerisations.

(b) We may further consider the possibility of *isomerisation* or saturation of the unsaturated nuclei, by which they lose their capacity of further growth. The doubly unsaturated radical formed by two monomeric styrene molecules can, for instance, be converted into a saturated molecule in one of the following two ways:—



Analogous possibilities exist for longer chains also, so that the breaking of reaction chains by intramolecular isomerisation or by ring-formation must be taken into account in a full discussion of the kinetics of polymerisation. As shown by the above formulae, the isomerisation occurs by a hydrogen atom wandering along the chain. It is finally fixed on one end of the chain, a double-bond being formed simultaneously on the opposite end. From this mechanism we may reasonably expect the velocity of isomerisation to become smaller with growing chain-length. In this way, a relatively high number of short chains are stabilised and the proportion of short chains in the ultimate product of polymerisation increased.¹⁶ In analogy to what we know about intramolecular transformations in general, we may expect the dependence of the isomerisation velocity on temperature to be relatively small. In any case, its activation-energy will be much smaller than that connected with the formation of nuclei.

We have included the influence of the isomerisation upon the kinetics of the polymerisation into the following formulae, under certain plausible assumptions, and for the case of a bimolecular formation of nuclei.

(c) We must not completely neglect the possibility of newly-formed long-chain molecules dissociating again, especially if the temperature of polymerisation is somewhat high and the chains already long enough. As already pointed out by Staudinger, and confirmed by many recent investigations, the large molecules are not comparable in stability with the small ones; they must therefore dissociate at relatively low temperatures. Still, we may reasonably doubt whether any perceptible dissociation really occurs at temperatures between 100° and 200° C.; but only special experiments could definitely answer this question. In the meantime, it appears necessary to include this effect into the general theory of polymerisation. Very conveniently, there exists a detailed investigation by W. Kuhn¹⁷ of the dissociation of long chains.

¹⁸ An analogous reasoning can also be used in the case of ring-formation. In connection with this problem we are developing a detailed theory of the kinetics of ring-formation from the point of view of intramolecular statistics.

¹⁷ W. Kuhn, *Ber.*, 1930, 63, 1503.

made as a part of an extensive work undertaken by him together with K. Freudenberg and concerned with the hydrolysis of the cellulose.¹⁸ In this paper by Kuhn, formulae are given for the dissociation-velocity of long chains under different conditions. Part of them can be directly applied to the thermal de-polymerisation of chain-molecules, whereas another part requires only small adjustments to be used to this purpose. The formation and dissociation of chains lead to an equilibrium dependent on temperature and on the molecular properties of the substance in question. The equilibrium constant can be represented in terms of the collision factors and the activation energies of both reactions.

(d) Another important complication, which may have a great influence on the properties of the products of the polymerisation, occurs when the nuclei still contain double bonds. This is the case with a great number of polymerising substances, as, for instance, with butadiene, isoprene, dimethyl-butadiene and chloroprene—as well as with those compounds which are known as “synthetic rubbers,” in consideration of their elastic properties. The experiments show, that nuclei of this kind may have their double bonds reduced to single bonds by appropriate activation, thermal or catalytic; the valencies which are set free in this way are used for linking the chains together, the result being the formation of a two- or three-dimensional lattice.* The products which are thus obtained have properties entirely different from those of the ordinary chain polymers, especially in regard to solubility, melting-point and elasticity. We must therefore introduce into our equations a *velocity of space filling*, in addition to the velocity of chain-growth, in order to take into account a side-reaction which may become so important under suitable conditions. The results obtained by Carothers and collaborators in the study of chloroprene show that a thermal space filling is a process highly dependent on catalysts. Since it involves an activation of the double bond, we may expect the same catalysts to be active in this case as we found to accelerate the formation of polymerisation-nuclei. This conclusion is, so far, confirmed by experiment. In the absence of catalysts,¹⁹ the activation energy of space filling may be supposed to amount to about 30-50 k. cal. per mol.—i.e. equal to that of the formation of the nuclei. It appears, furthermore, plausible to suppose the probability of a chain taking part in a space filling to be proportional to the number of double bonds present in it. In the case of the above-mentioned substances, this means a proportionality to the chain-length. The velocity of space filling must therefore grow very quickly (exponentially) with increasing temperature, and gradually (linearly) with increasing chain-length. Both these conclusions accord with experiment. The inclusion of the space filling reactions into the mathematical scheme of the polymerisation process seems to offer no insuperable difficulties. We have started calculations of this kind and will communicate them as soon as they are completed.

¹⁸ Compare especially K. Freudenberg, *Tannin, Cellulose, Lignin*, Springer, 1933, p. 97.

* We shall hereafter refer to this as “space filling.”

¹⁹ Stress must be laid again on the fact, that it is extremely difficult to exclude practically the smallest traces of catalytically active substances. This is of practical bearing for instance in the technical production of different polymers of chloroprene (α , β , μ , ω —polymers).

2. Discussion of the Kinetics of Polymerisation.

It is not difficult to derive approximate formulae for the velocity of the reactions discussed qualitatively in the previous section. According to what has been said above, we have to consider separately the cases of a bimolecular and of a monomolecular formation of the nuclei.

We will denote by \mathbf{H} the molecules of the non-activated monomeric substance, and by \mathbf{H}_j those of the polymeric radicals built up from j simple molecules. All \mathbf{H}_j we consider, as described in the previous section, to be non-saturated, and able to grow further by addition of more molecules of \mathbf{H} .

The *monomolecular* mechanism by which an active nucleus is produced, can be described by the formula



where x denotes the energy which is necessary for the production of the nucleus. As mentioned above, this energy is usually somewhat high. \mathbf{H}_1 denotes the newly-formed polymerisation-nucleus. Its further development can be described by the following set of formulae :

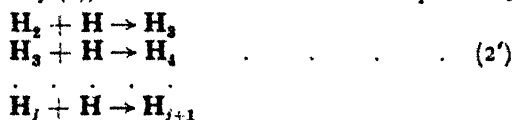


All the reactions (2) require only a small activation-energy and therefore proceed much more quickly than reaction (1). For the sake of simplicity we will assume that the velocity constant of all the reactions (2) is the same. The velocity constant of reaction (1) is smaller by 3 to 6 orders of magnitude.

The *bimolecular* formation of nuclei is described by the formula



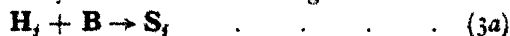
The first polymerisation-nucleus is in this case the dimeric radical \mathbf{H}_2 . Its growth is again represented by (2), under omission of the first equation :



In both cases, we have to supplement (1) and (2) by a formula representing the slow stabilisation of the radicals \mathbf{H}_j and the formation of stable chain-molecules \mathbf{S}_j :—

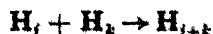


The stabilisation may also occur by collision with a foreign molecule \mathbf{B} :—



Since \mathbf{S}_j is supposed to be incapable of growing any further, reaction (3) and (3a) inhibit the polymerisation. The substances \mathbf{B} thus act as *negative catalysts*.

We neglected in this scheme reactions of the type of



which we discussed in the previous section. We did not do this because we supposed them not to occur at all or to be improbable from the kinetic point of view, but only because we found that their occurrence

does not appreciably change the general course of the polymerisation-process. This is suggested by the results discussed below.

The reactions (1), (2), (3) or (1), (2) and (3a) together form a typical reaction chain. All that is known about polymerisation agrees with the supposition that they are chain reactions. The chain structure of the polymers itself points in this direction.

The assumption of reaction chains is further supported by the occurrence of positive and negative catalysis. Negative catalysis is easily explained by reaction (3a), whereas positive catalysis is to be explained by a catalytic acceleration of reaction (1). The almost explosive manner in which many polymerisations take place is characteristic of chain reactions. The polymerisation of styrene and of acrylic ester is, for instance, accompanied by an intense foaming. A finer detail which fits well into the picture is the existence of an induction period (mentioned above). Calculations based on formulae (1-3) in fact lead to the prediction of an induction-time.

We shall denote the quantity of the initial substance **H** present at a given moment by M , the amounts of the radicals **H**, either by M_{j-1} (in the "monomolecular" case), or by M_j (in the bimolecular case). The initial concentration of **H** (at $t=0$) we put equal to 1. By an appropriate choice of units, the reaction-constant of process (2) can also be made equal to 1. The velocity-constant of reaction (1), which we denote by a , is in this case equal to something between 10^{-3} and 10^{-6} . Irrespective of the units chosen, a has the meaning of the relation between the velocity-constants of (1) and (2). The stabilisation reactions (3) and (3a) will be disregarded for the moment.

(a) The Nuclei are Formed Monomolecularly.

The differential equations for (1) and (2) occurring together are in this case—the amount of **H**, being denoted by M_{j-1} —as follows:—

$$\begin{aligned}\frac{dM_2}{dt} &= aM - MM_2 \\ \frac{dM_3}{dt} &= MM_2 - MM_3 \\ \frac{dM_4}{dt} &= MM_3 - MM_4 \\ &\vdots \\ \frac{dM_n}{dt} &= MM_{n-1} - MM_n \\ &\vdots \\ Mdt &= dz \quad \quad \quad (4)\end{aligned}$$

Putting
we obtain:—

$$\begin{aligned}\frac{dM_2}{dz} &= a - M_2 \\ \frac{dM_3}{dz} &= M_2 - M \\ \frac{dM_4}{dz} &= M_3 - M_4 \\ &\vdots \\ \frac{dM_n}{dz} &= M_{n-1} - M_n\end{aligned} \quad \quad \quad (6)$$

The transformation (5), leading from (4) to (6), means the introduction of a new time-factor z , which becomes greater with progressing reaction. We shall call z the *individual time* (Eigenzeit) of the reaction. For $t = 0$, also, we put $z = 0$ too. The solution of the equations (6), with appropriate initial conditions, is

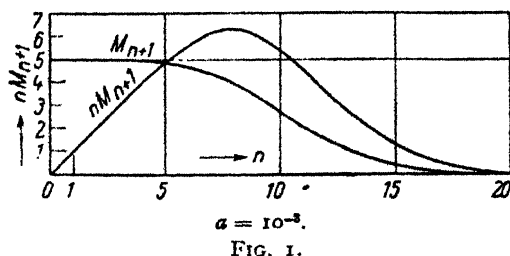


FIG. 1.

$$M_n = ae^{-z} \sum_{p=n-1}^{\infty} \frac{z^p}{p!} \quad (7)$$

Obviously, $M_2 > M_3 > M_4 > \dots$. With increasing z , the right side of (7) becomes less and less different from the expression:

$$ag(n, z) = \begin{cases} a & n-1 \leq z \\ 0 & n-1 > z \end{cases} \quad (8)$$

Using (8) instead of (7), we imply that the chains grow with a uniform velocity (referred to the time-scale z)—a result which appears immediately plausible. The discontinuity expressed by (8) is practically smoothed over by statistical scattering—that is why the correct formula is (7) and not (8).

For the amount of the non-polymerised substance M , we obtain:

$$M = 1 - az - \frac{az^2}{2} \quad (9)$$

The solution $z = z_{\infty}$ of the equation represents the value of the individual time z after which the initial substance is completely used up. To the first approximation, z_{∞} is given by $\sqrt{\frac{2}{a}}$. The individual time z_{∞} , of course, corresponds to $t = \infty$ on the ordinary time-scale. Introducing (9) into (5), we obtain

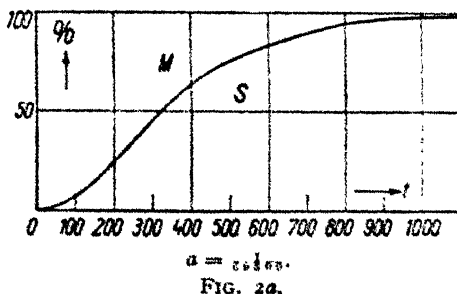


FIG. 2a.

$$\frac{dz}{dt} = 1 - az - \frac{az^2}{2} \quad (10)$$

as the relation between the individual (z) and the ordinary (t) time. The values of M_n which we obtain from (7) in putting $z = z_{\infty}$ represent the

final quantities of the different polymers. The chain length which is present to the highest amount in the mixture is approximately equal

to $0.9z_{\infty} = 0.9\sqrt{\frac{2}{a}}$. (With (8) it would be z_{∞} exactly).

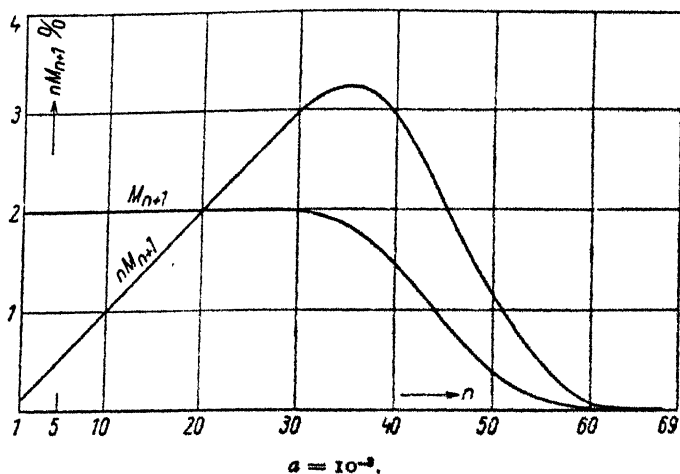


FIG. 3.

Fig. 1 shows the distribution of chain-lengths to a time $z = 10$, corresponding to an early stage of polymerisation. Figs. 2 and 2a show the amount of polymerised substance S , as a function of the time t .

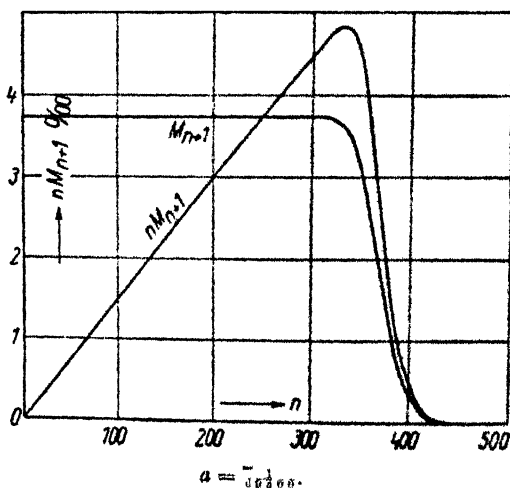


FIG. 3a.

Figs. 3 and 3a represent the final distributions of the chain-lengths, at $t = \infty$.

The formulae given so far are exact. The following are only approximate.

(b) The Nuclei are Formed Bimolecularly.

The differential equations corresponding to (1) are now :—

$$\begin{aligned}\frac{dM_2}{dt} &= aM^2 - MM_2 \\ \frac{dM_3}{dt} &= MM_2 - MM_3 \\ &\dots \dots \dots \\ \frac{dM_n}{dt} &= MM_{n-1} - MM_n \\ &\dots \dots \dots\end{aligned}\quad (11)$$

In introducing again the individual time z , when using relation (5) instead of the ordinary time t , we obtain :—

$$\begin{aligned}\frac{dM_2}{dz} &= aM - M_2 \\ \frac{dM_3}{dz} &= M_2 - M_3 \\ &\dots \dots \dots \\ \frac{dM_n}{dz} &= M_{n-1} - M_n\end{aligned}\quad (12)$$

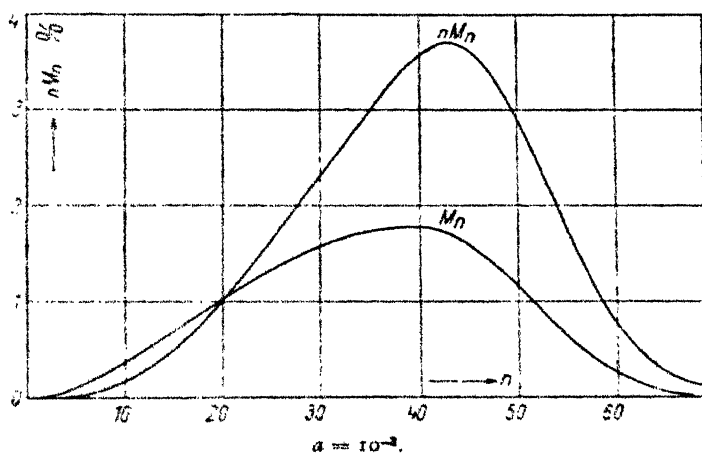


FIG. 4.

The solutions of (9) are :—

$$M_n = ae^{-z} \sum_{p=n-1}^{\infty} \frac{z^p}{p!} - \begin{cases} \frac{a^2}{2}(z-n)^2 & \dots n < z \\ 0 & \dots n > z \end{cases} \quad (13)$$

and

$$M = 1 - 2az - \frac{az^2}{2} + \frac{a^2z^4}{24} \quad (14)$$

The value z_{∞} which corresponds to a given a is now greater by about $\frac{1}{8}$, viz. $\frac{9}{8}\sqrt{\frac{2}{a}}$. Figs. 4 and 4a are examples of the final distributions of the

chain-lengths. Figs. 2 and 2*a*, representing polymerisation as a function of time, remain valid in this case too. The existence of an induction period is clearly shown by these graphs. The most favoured chain-length is again equal to about $0.9 z_{\infty}$ —which now means $0.9 \times \frac{9}{8}\sqrt{\frac{2}{a}}$.

(c) The Influence of the Stabilisation Reaction (3).

We supplement now the above discussed scheme by the reaction (3), with a velocity-constant b of its own, supposed to be independent of j . What is the final distribution $\mathcal{F}_j(z_{\infty})$ of the S_j -values at $z = z_{\infty}$ (or $t = \infty$). If b is so small that reaction (3) intervenes only when the polymerisation is practically completed, then the distribution curve must practically coincide with the former curve $M_n(z_{\infty})$. In all other cases, the number of shorter chains is increased and that of the longer chains diminished by the intervention of reaction (3).

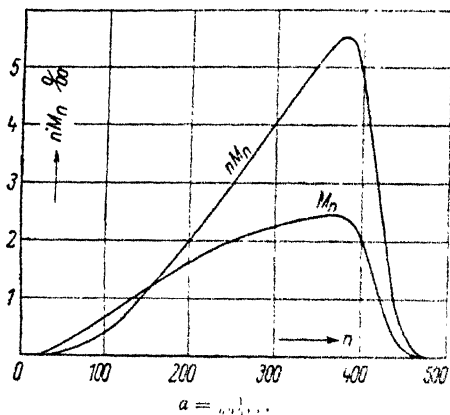


FIG. 4a.

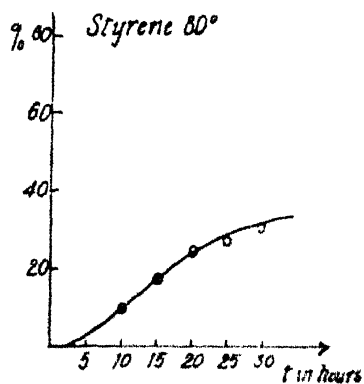


FIG. 5.

On the assumption of a bimolecular formation of nuclei we obtain:—

$$\mathcal{F}_n(z_{\infty}) = \left(\frac{2z_{\infty} - n}{2z_{\infty}} \right)^{\frac{\pi b}{4\sqrt{a}}} M_n(z_{\infty}) + \begin{cases} (\pi b \sqrt{a} \cos \sqrt{a}n \dots n < z \\ 0 \dots n > z \end{cases} \quad (15)$$

This formula holds, however, only if $\frac{\pi b}{4\sqrt{a}}$ is much smaller than 1. Because $n > 1$ the factor which stands before M_n is smaller than 1 and the first term therefore smaller than M_n ; the second term increases the relative probability of the short chains.

Negative catalysis of the type (3*a*) fits into the same scheme so long as the concentration of the catalyst does not decrease appreciably in the course of the polymerisation—i.e. so long as the stabilisation (3*a*) obeys formally a monomolecular law.

3. Comparison of the Theory with the Experimental Results.

On comparing the experimental curves 5 and 5*a*, which describe the polymerisation of styrene as a function of time, with the "theoretical" curves in Figs. 2 and 2*a*, we observe a general agreement in their shape:

an induction-period is followed by a linear section of the curve, which finally becomes concave and approaches the horizontal when the polymerisation is nearing completion. We may therefore say that the theory describes the process of polymerisation in an essentially correct way.

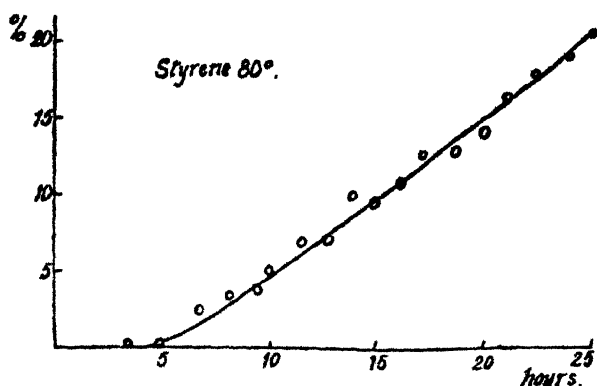


FIG. 5a.

A more detailed analysis reveals that whereas theory predicts a relatively long induction period (lasting until about 10-15 per cent. of the substance is transformed), the experimental induction times are apparently much shorter. In many cases, for instance, in those of indene and of dimethyl butadiene (Figs. 6, 7 and 8), there appears to be no induction period at all.

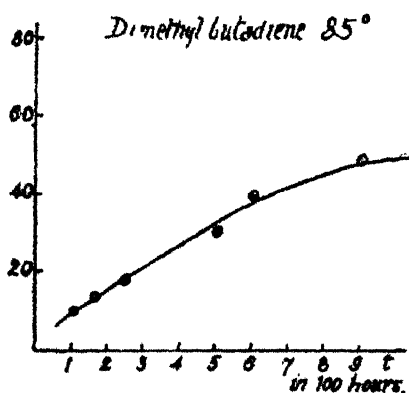


FIG. 6.

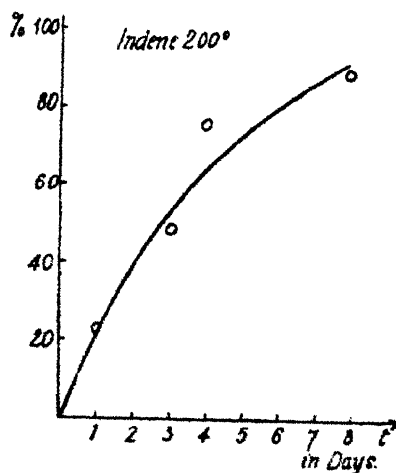


FIG. 7.

In order to show how far the theoretical equations are capable of representing the experimental results, we plotted together, in Fig. 9, the theoretical curve for $a = 10^{-3}$, and the experimental results obtained with styrene at 80°.

We must remember here, that measurements in the liquid phase are not very appropriate for comparison with the theory. The single chain growth reactions are exothermic; the temperature shown by a thermometer immersed in the reacting liquid is therefore not identical with that

prevailing in the immediate neighbourhood of the reacting molecule. We must suppose, on the contrary, that the temperature of the polymerising substance

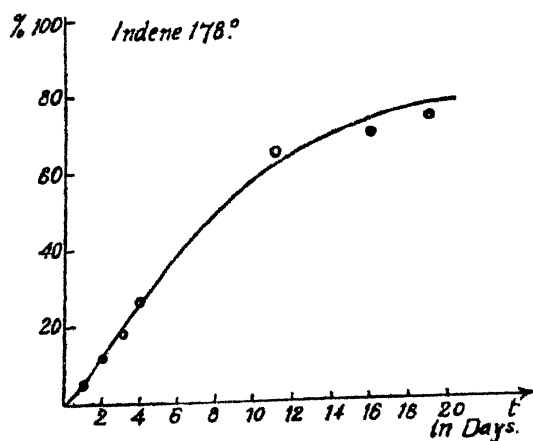


FIG. 8.

itself is often much higher than the mean temperature of the liquid, thus permitting a much higher velocity of formation of the nuclei and making the induction period shorter. Moreover, we must remember that small amounts of catalytically active substances may increase the initial velocity of the formation of nuclei and thus also reduce the induction period. Measurements of the polymerisation velocity in solutions can be expected to give results more appropriate for comparison with the theoretical curves. Unhappily, these measurements are not yet carried so far as to enable their results to be used in this discussion.

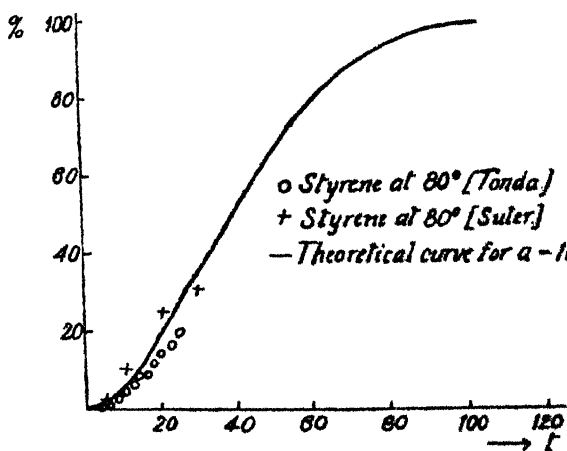


FIG. 9.

Summary.

(1) The kinetics of polymerisation processes are discussed from the point of view of a slow nucleus-forming reaction, followed by a quick growth of the chains.

(2) The following side-reactions are discussed :—

- (a) Isomerisation.
- (b) Dissociation of chains.
- (c) Intercombination of nuclei.
- (d) Formation of lattice.

(3) The influence of catalysts on both stages of the main reaction is considered.

(4) Formulae are derived for the above polymerisation-mechanism, both for a monomolecular and for a bimolecular formation of nuclei.

(5) The influence of isomerisation is introduced into the formulae.

(6) The theoretical results are compared with the experiments, so far as this appears possible to-day. The comparison reveals that the simple theoretical mechanism corresponds qualitatively to the experimental picture, and is even able to reproduce the experiments with styrene quantitatively with a high degree of accuracy. In discussing the finer details of the polymerisation-processes, however, the side-reactions mentioned under (3) must undoubtedly be taken into consideration too.

Wien: 1. Chemisches Universitäts-Laboratorium.

GENERAL DISCUSSION

Dr. Albert Wassermann (London) said: In studying bimolecular reactions of the type $a + b \rightarrow c$, it is sometimes observed that the constant Z of the Arrhenius equation $k = Ze^{-E/RT}$ decreases rapidly as the number of atoms of which the molecules a and b consist is increased.²⁰ The figures given below represent a good example:—

KINETICS OF DIENE SYNTHESSES (ADDITION OF QUINONES TO *cyclopentadiene*); BENZENE SOLUTION.

No.	(a).	(b).	(c).	Z ²¹ .	E ²¹ .
1	$C_6H_4O_2$	C_5H_6	<i>cyclopentadiene</i> Benzoquinone	1×10^6	11.6
2	$C_{10}H_8O_2$	C_8H_8	<i>cyclopentadiene</i> α -Naphthquinone	7×10^4	10
3	$C_{11}H_{10}O_2$	C_8H_8	Di- <i>cyclopentadiene</i> Benzoquinone	3×10^4	13

The Z value of the reaction ethylene + ethylene ($a = b = C_2H_4$) amounts, according to Pease,²² to 2×10^8 . It can be seen that the Z values of the diene syntheses (reacting molecules containing 12–23 atoms) are much smaller. The difference is so large that it might be wondered how the formation of highly polymerised compounds occurs at all. The possibility of the synthesis of these compounds must evidently depend not only on a very low activation energy.²³ The "temperature independent factor" Z of the Arrhenius equation must also be increased in some "abnormal" manner under certain experimental conditions.

Dr. J. H. de Boer (Eindhoven) said: The mechanism of growth of the nuclei and the chains by an addition process of monomeric molecules on the top of the chains with a high velocity brings to mind the process of crystal growth, e.g., of mercury crystals in the classical experiment of Volmer and Estermann. Now, in these latter cases the velocity of growth is large because a large number of the atoms or molecules striking the sides of the growing needle-crystal are loosely bound there by adsorption forces

²⁰ Cf. Evans and Polanyi, *Trans. Faraday Soc.*, 1935, **31**, 875; Eyring, *J. Chem. Physics*, 1935, **3**, 107. Cf. also Rice and Gershinowitz, *ibid.*, 1934, **2**, 853.

²¹ The dimension of Z is 1/g.-mol.-sec. and that of E is Cal.

²² *J. A. C. S.*, 1932, **54**, 1876.

²³ It should be borne in mind that the activation energy of the association of two triphenylmethyl molecules is 8 Cal.

and migrate to the top, where they contribute to the lengthwise growth. Is such a mechanism possible, also, in the case of the growing polymers?

Dr. D. Finlayson (*Long Eaton*) said: Reference has been made to the fact that the rate of growth of long-chain compounds is greater than would be expected from the standpoint of the conventional theories. The explanation of this must be looked for on lines other than those so far considered, and in this connection, I would suggest that Dr. Carothers' remarks about the analogies between vital growth and the process of polymerisation are worthy of the closest study.

In both processes, long-chain molecular complexes, in suitable environments which contain molecules fundamentally of the same nature as those forming the units in the molecular chains, are able to grow by a series of chemical interactions between the end of the chain and the appropriate molecules of the environment. These processes differ from ordinary crystallisation mainly in that the mechanism by which the correct molecules are selected from the environment, and suitably oriented with respect to the molecules at the end of the chain, would appear to be rather more complicated. I suggest that the mechanism of selection and orientation is as follows.

Any molecular chain is necessarily in a state of active vibration before growth can occur. The energy to initiate and maintain the necessary intensity of vibration may be derived either from thermal collisions with the material of the environment or from an external source of radiant energy. The vibrations thus acquired by the molecular chain will be received in a series of impulses which may, or may not, have some connection with the natural vibration period of the unit of the molecular chain. In either case, these impulses will travel as series of waves backwards and forwards along the molecular chain, and the resulting motion may be regarded as the superposition of a random motion on the fundamental and harmonic vibrations of the molecular units of the chain. For our purpose, the random motion may be neglected; the important point is that a series of random impulses is able to stimulate a chain to vibrate with its own natural vibrations (on which are superposed other random oscillations).

When these natural vibrations reach a free end of the molecular chain, they must (as in sound waves at the open end of a pipe) partly return along the chain with diminished intensity, and partly tend to dissipate themselves in the surrounding medium. In other words, a long-chain molecular complex tends to produce, continuously, in the medium at the end of the chain a vibration "like" that of the unit of the chain itself. The effect of this will be to orientate the molecules of the medium at the end of the chain in such a way as to make it possible for the vibration to be transmitted, *i.e.*, the molecules of the medium will present themselves to the end of the chain in the configuration of the units of the chain themselves. It is thus that, I imagine, growth will occur.

It has been remarked that any rational explanation of polymerisation must also explain depolymerisation. It may be suggested that the mechanisms of both processes are, essentially, the same.

When a long-chain compound is "deprived of its food," or placed in an environment which does not contain any "like" molecules capable of dissipating its characteristic vibrations, the amplitude of these vibrations must, in general, increase. The result will be that, from time to time, certain molecular chains will acquire amplitudes of vibration greater than they are able to withstand, and these chains will be torn asunder, the most probable positions of rupture being near the centre of each chain. Thus, in simple long-chain compounds, as in complex living organisms, the absence of opportunity for growth, in time, results in death.

Dr. R. Spence (*Leeds*) said: Some three years ago, I studied the polymerisation of gaseous formaldehyde in pyrex vessels at room temperature.²⁴ The pressure decreased at first unimolecularly, then bimolecularly, and

²⁴ Spence, *J. Chem. Soc.*, 1933, 1193.

finally the rate slowed down according to a higher order. The nature of the polymeric deposit is of some interest in connection with Dr. de Boer's suggestion that there might be a surface diffusion to the centres of growth. Most of the glass surface appeared to be covered with a thin translucent film of varying thickness, in addition to which small nodules could be observed, sometimes reaching 2 mm. in diameter. Furthermore, the velocity of polymerisation was closely proportional to the area of surface present, and it might be supposed that the rate depended upon the degree of adsorption of the formaldehyde upon the polymer and the diffusion of the adsorbed molecules to the active centres. The kinetic data, on the other hand, do not support this view, but indicate rather that the rate depends upon the number of active centres present. It is of interest to note that growth appears to continue on the same regions of the deposit in consecutive experiments in spite of evacuation and the lapse of time between them.²⁵ Accordingly, two kinds of activity may be involved, namely that associated with the growing chain, and a more permanent type capable of initiating new growth.

Dr. E. Heymann (London) said: Professor Mark asks how one could determine the distribution of molecular weights in a solution of polymers which contains molecules of different molecular weight (or chain-length).

Let us assume we have three different groups of molecules of different chain-length (or molecular weight), and let us furthermore assume, that these molecules are dipoles. If these are exposed to an alternating electric field, there are characteristic frequencies γ for each group of molecules, at which they become oriented in the field. The critical frequency (wave-length λ) will be the smaller (λ higher), the larger the molecules (Debye).²⁶ If, therefore, we measure the dielectric constant ϵ , in relation to the wave-length, we find for small wave-lengths the dielectric constant of the pure solvent (ϵ_0). If we increase the wave-length to a certain value, the smallest molecules will be oriented in the field, and thus contribute to the orientation polarisation, that is to say, we observe a rise in dielectric constant (ϵ_1). If we increase the wave-length further, we shall come to a region where the molecules of larger size become oriented, and consequently, we shall observe a second rise in dielectric constant (ϵ_2). With further increase in wave-length the largest molecules will contribute to the orientation polarisation and the dielectric constant will rise again (ϵ_3) (Fig. 10). That is to say, for every group of molecules there corresponds a dispersion region in the ϵ - γ curve. In practice, the conditions will often be more difficult, since the mixture need not necessarily contain distinct groups of molecular weights. If the molecular weights are very close together, it will not be possible to distinguish between the single dispersion regions, which in this case will grow together to one very broad region, in which the dielectric constant increases slowly with increasing wave-length.

It is true that dielectric constant measurement with variation of wave-length involves experimental difficulties, especially if small wave-lengths are required. Molecules of colloidal dimensions correspond to wave-lengths between about 5 and several 100 metres. Other complications may arise, if the dipole is not fixed in the molecule or if a part of the molecule is oriented independently or almost independently (as suggested by Professor K. H. Meyer). In any case, I think that it is worth trying the dielectric-constant method for getting information about the distribution of molecular sizes in solutions of highly polymerised substances, especially as a similar method has been suggested by N. Marinenco,²⁷ and by J. Errera and his co-workers²⁸ to determine the molecular weights of proteins in solution.

²⁵ Cf. Carothers, this vol., page 39.

²⁶ P. Debye, *Polar Molecules*.

²⁷ N. Marinenco, *J. Chim. Physique*, 1927, **24**, 572; 1931, **28**, (2), 76; *Compt. rend.*, 1929, 188, 1163; *Compt. rend. Soc. Biol.*, 1930, **103**, 872; *Koll. Z.*, 1932, **58**, 285.

²⁸ J. Errera, *J. Chim. Physique*, 1932, **29**, 575; B. M. Bloch and J. Errera, *Physik. Z.*, 1933, **33**, 767.

Dr. E. A. Moelwyn-Hughes (*Cambridge*) said: If, in the present reaction, the disparity between the behaviour in the gas phase and in solution can be adduced as evidence for the mechanism outlined by Professor Rideal and Professor Mark, then the results of Abkin and Medvedev (p. 286) would appear to indicate quite a different mechanism for the sodium-catalysed polymerisation of butadiene.

Professor H. Mark (*Wien*), in reply, said: To save time I will discuss together the most interesting results of Dr. Wassermann and the very striking remark of Dr. de Boer. In both cases the question is how does the rate of chain growth depend upon the length of the chain? a point which seems to me to be fundamental in the kinetics of polymerisation reactions. In our contribution Dr. Dostal and I made our first calculations on the assumption that the growth constant of a growing chain would be independent of its actual length. This procedure, which must be, of course, taken as a first approximation, seemed to be justified to a certain extent by the fact that one generally can assume that, with increasing chain-length, the heat of activation and the steric factor for the next elementary addition process both decrease. It can happen, as Professor Rideal has

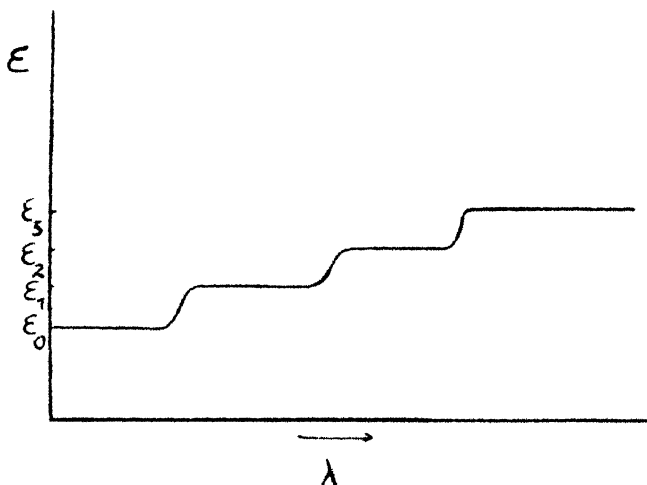


FIG. 10.

already pointed out, that these two influences more or less compensate one another. This may be the case, but it does not necessarily follow. It was therefore necessary to improve the calculation as to the building up of long chains, and to work out a formula, which includes a certain variability of the chain growth constant. Dr. Dostal was able to show that one can accomplish the calculation also for the fact that K_n is not constant, but depends upon n . For the dependence of the reaction constant upon the chain-length, one has put $K_n = A \cdot \alpha^n$ where n is the number of the members of the chain and A and α are constants.

This equation allows the assumption of an increasing or decreasing probability for the next step with growing chain-length.²⁹

It is probable that, in most cases, the rate of growth will decrease with increasing chain-length because the energy of activation of the growing reaction is already so small, when the chains are short, that its decrease during the growth cannot very much affect the velocity of the reaction. On the other hand, there are very good reasons to assume that the steric factor will decrease very rapidly, when the size of the reacting molecules

²⁹ See also Dr. Dostal's remarks concerning Dr. Bawn's paper, p. 183.

increases. All our knowledge of the kinetics of bimolecular reactions in the gaseous state (and particularly also in dilute solutions), the experiments mentioned by Dr. Wassermann, and last but not least, the theoretical considerations of Eyring, Evans and Polanyi, and the recent work of Hellmann and Syrkin, show that the steric factor of a bimolecular reaction may decrease to 10^{-2} , when the reacting molecules have a considerable size. The reason for this behaviour is (as Dr. Bawn will point out in his paper) not so much geometrical considerations, as the fact that we have an interaction of oscillating systems, which obey the laws of quantum mechanics and have to fulfil different conditions, if a mutual reaction is to be allowed. One should therefore assume that, generally, the chain-growth constant should decrease very rapidly with increasing chain-length; this leads to the result that long chains could not be built at all. Experiment shows very clearly, on the contrary, that they are formed in nearly every case when polymerisation takes place at all.

In connection to the contribution of Dr. de Boer, I would add that it seems quite possible that some kind of adsorption of the monomeric molecule on the surface of the polymeric macromolecule plays a similar rôle, as it does in the case of crystal growth. Therefore the analogy, which Dr. de Boer has pointed out seems to me to be very reasonable, and the idea of Volmer, which was so useful in the case of crystal growth, may be of the same use in the growth of long chain molecules. In fact, similar processes have already been taken into account. Dr. Medvedev refers to this in his contribution, where he meets a similar difficulty from an "activation" of the monomeric through the polymeric macromolecule.

To what extent such an activation may be due to surface processes, as Dr. de Boer suggested, will only be cleared up by very careful quantitative analysis of polymerisation reactions: this is not at all easy, and must be worked out with the greatest care for every single polymerisation substance.

In reply to a remark by Dr. Kienle, I would like to point out, that in the case of the esterification of polyvalent alcohols with polybasic acids and in the case of the mutual esterification of ω -oxycarbonic acids the reactions which respectively start the chain and propagate the chain are essentially of the same type. It therefore seems probable that they have reaction rates of the same order of magnitude. Of course, one has to take in account, that the growth reaction will decrease in rapidity with increasing chain-length, while the "starting" reaction will be independent of the extent of condensation. In any case, there is no reason for a very rapid growth-reaction, so that it may be better to speak not of a chain-reaction but of a step-reaction. In such a type of reaction one does not get so long chains as in the case of very rapid growth, and one has to expect always to find a somewhat large amount of intermediate products, i.e., chains of medium length, as Dr. Kienle has pointed out. This seems also to account for the fact, which especially Staudinger mentions, that one gets chain-like condensation products mostly only in the hemicolloid state, and does not reach really high polymeric specimens. The rate of building up nuclei is here of the same order of magnitude as the velocity of growth, and the large number of nuclei formed per unit of volume and time is always competing with the growing chains, with the result that very long molecules cannot be built.

THE KINETICS OF LONG CHAIN DISINTEGRATION APPLIED TO CELLULOSE AND STARCH.

BY PROFESSOR KARL FREUDENBERG (*Heidelberg*).

Received 7th August, 1935.

In 1921 evidence was given in favour of the concept that cellulose is a long chain molecule of *equally* linked glucose residues.¹ The reasoning was based on the kinetics of long chain disintegration. The maximum yield of cellobiose, from such a system, would exceed 30 per cent. but would never reach 100 per cent.; under certain circumstances it would approach 67 per cent. This was confirmed by experiment.

It was later found that cellulose when hydrolysed with 50 per cent. sulphuric acid at 18° has a lower velocity of reaction than cellobiose ($K_n = 0.36 \times 10^{-4}$, $K_2 = 1.07 \times 10^{-4}$, K_n being the velocity in the first stage of cellulose hydrolysis, K_2 the constant of cellobiose).² Werner Kuhn carried out the calculation of the process³ on the assumption that the velocities K_3 , K_4 , etc., with which cellotriose, cellotetraose, etc., are attacked at the incipient hydrolysis, lies between K_2 and K_n . The calculations are in good agreement with the experimental curve. Werner Kuhn's formulæ are also the basis for the calculation of disintegration processes of all other long chain molecules.

The experiments mentioned were based on the iodometric estimation of the aldehyde group. When the optical rotatory power is observed during hydrolysis, similar curves are obtained, which could also be calculated by additive formulæ: also given by Werner Kuhn.

In connection with these experiments it was found that the molecular optical rotation of biose, triose, tetraose, etc., is additive and leads to the rotation of the polysaccharide by a linear function.⁴ This fact has been explained by optical superposition and has been confirmed for cellulose and starch and their methyl derivatives. It has been, so far, the strongest evidence for the fact, that in cello-biose, -triose, and -tetraose, as well as in cellulose itself, only *one* kind of linkage occurs, which is uniform in structural and configurational aspect. Methyl-starch and its methylated oligosaccharides behave in the same manner.

The uniformity of the cellulose bond has now been confirmed by G. Blomqvist. He determined the velocity of hydrolysis of L. Zeche-meister's cellotriose and cellotetraose. K_3 and K_4 (incipient velocity at 18° C.) are 0.636×10^{-4} and 0.506×10^{-4} respectively. The former experiments have been repeated and completed, the figures being now:

¹ K. Freudenberg, *Ber.*, 1921, **54**, 767. Compare my pamphlet: *Tannin, Cellulose, Lignin*, Berlin, 1933.

² K. Freudenberg, Werner Kuhn and collaborators, *Ber.*, 1930, **63**, 1510.

³ W. Kuhn, *Ber.*, 1930, **63**, 1503; *Z. physik. Chem. A.*, 1932, **159**, 368; *Ber.*, 1932, **65**, 484.

⁴ K. Freudenberg, K. Friedrich, T. Bumann, *Ann.*, 1932, **494**, 41.

	Cellulose.		Starch.	
	18°.	30°.	18°.	30°.
K_2 . .	1.07×10^{-4}	6.94×10^{-4}	1.43×10^{-4}	10.3×10^{-4}
K_3 . .	0.636 "	4.50 "	—	—
K_4 . .	0.506 "	3.65 "	—	—
K_n . .	0.305 "	2.34 "	0.97 "	7.0 "

From these figures the heat of activation U and the steric factor A may be approximately calculated.

	Cellobiose.	Cellotriose.	Cellotetraose.	Cellulose.	Maltose.	Starch.
U . . .	27.300	28.600	28.900	29.800	28.800	28.900
$A \times 10^{-16}$.	3.4	18	24	67	64	52

The velocities of hydrolysis of cellotriose and -tetraose lie between those of cellobiose and cellulose, indicating once more that a continuous sequence leads from biose over the oligosaccharides to the polysaccharide. The crystalline cellodextrine of M. Bergmann and of K. Hess, formerly called bioseanhydride or biosane, fits into this series. Its degree of polymerisation may be assumed to be about 30.

The assumption made by Werner Kuhn for the calculation of the hydrolysis of polysaccharides has therefore been confirmed by experiment.⁵

The figures obtained with the two main constituents of potato starch indicate that amylo-amylose possessed a lower average degree of polymerisation than amylo-pectin. Both preparations are mixtures of polymer homologues, representing fairly long chains. The optical behaviour is in agreement with this conclusion.

GENERAL DISCUSSION

Professor H. Mark (*Wien*) said: Table II. contains a result which is of interest in connection with our general knowledge of high polymeric substances. One assumes generally (and, so far as one can see, also in agreement with experiment) that long chain molecules dissociate more readily with increasing chain-length. In contradiction to this, the measurements of Freudenberg show that the activation energy of the hydrolysis of cellulose is distinctly greater than that of cellobiose, cellotriose and cellotetraose. This may be due to the fact, that the hydrolysis of cellulose does not take place in a really homogeneous medium, but that one has a degradation in the swollen state. It may be that the glucosidic oxygen-link is strengthened by its position in the lattice; this would mean, that during the growth process of cellulose a certain gain of energy takes place.

Dr. E. A. Moelwyn-Hughes (*Cambridge*) said: The critical increment for the hydrolysis of cellobiose (27,300 calories) is the only one which deviates markedly from the mean critical increment (29,000) for the remaining reactions to which the data in Professor Freudenberg's second table refer.

⁵ A. af Ekenstam (*Svensk Kem. Tidskr.*, 1934, 46, 157) states that in 65 per cent. sulphuric acid solution cellulose hydrolyses on the lines of a monomolecular process. By repeating his experiment we were unable to confirm his results. His assumption that 50 per cent. sulphuric acid is not an adequate medium can likewise not be accepted.

Combining his figures for the velocity of hydrolysis of this disaccharide at temperatures of 18° and 30° C. with my values,⁶ at 60° and 80° C., I find the velocity constants over the complete temperature range to be satisfactorily given by an expression where $E = 29,000$ calories. The two sets of experiments necessarily refer to systems containing different concentrations of catalyst, but independent experiments show that E is not sensitive to the concentration, so that the combination of the results is justified. The revised critical increment for the hydrolysis of cellobiose is thus in good agreement with the other values quoted in the paper, and strengthens Professor Freudenberg's argument. As Professor Haworth appreciated some years ago,⁷ the critical increment is a much more reliable guide to the structural stability of carbohydrates than is the velocity itself. Further evidence in support of this view is to be found by comparing the hydrolysis of derivatives of the normal glucoses, including cellulose and starch, with the hydrolysis of derivatives of the "active" glucoses, or substituted glucofuranoses. E for the former class appears to be insensitive to temperature, whereas E for the latter class falls with a rise in temperature.⁸

If we express the velocity constant for a bimolecular reaction in the form $k = P \cdot Z \cdot e^{-E/RT}$, where E is the Arrhenius critical increment and Z is the gas-kinetic collision frequency, it is found that P sometimes varies from reaction to reaction. There seems now a fairly general agreement to accept, provisionally, the classification of bimolecular reactions into those having fast, normal or slow rates, according as P exceeds, equals or is less than one. In point of time, the slow reactions were first discovered.⁹ The next set of reactions in solution to which kinetic considerations were applied were fast reactions.¹⁰ Finally, research among some of the oldest publications extant revealed the existence of a number of reactions with normal velocities.¹¹ This chronological recapitulation has been deemed necessary because the existence of the fast reactions has been almost consistently ignored in the recent discussions of the factor P . The new experimental material supplied by Professor Freudenberg in the present paper should freshen our memory to the fact that P is known experimentally to vary from 10^{-9} to 10^9 . These figures are not in any sense limiting values; they are simply the smallest and largest experimental magnitudes of which I am personally aware.

Professor K. Freudenberg (Heidelberg), in reply, wrote: It is true that the polypeptides of glycine are more readily hydrolysed with increasing chain-length. In the same way cellulose suffers acetolysis with acetic anhydride and sulphuric acid more readily than cellobiose. However, cold 50 per cent. sulphuric acid hydrolyses cellulose more slowly than cellobiose. It has been shown by experiment that cellobiose has a velocity constant lower than triose, and triose lower than tetraose. From this it follows that the behaviour of cellulose is not due to the way in which it is brought into solution, i.e., by heterogeneous conditions. I am convinced that the solution of cellulose is a true solution soon after dissolution, when the first titration is carried out, since the solution shows no viscosity.

The slower reaction of cellulose compared with that of the lower saccharides depends upon an increase of the activation energy, for the activation energy of the central groups is higher than that of the terminal groups. The phenomenon is based on the fact that the terminal groups are linked to the others by an affinity energetically different from that with which they are linked to central groups, whereas Professor Mark presumes equal energetic conditions for all linkages. This has already been discussed by W. Kuhn.¹²

⁶ *Trans. Faraday Soc.*, 1928, **24**, 309.

⁷ *Annual Reports on the Progress of Chemistry*, 1929.

⁸ *Z. physikal. Chem.*, 1934, **26B**, 281.

⁹ Christiansen, *ibid.*, 1924, **113A**, 35.

¹² *Chem. Reviews*, 1932, **10**, 240.

¹⁰ *Trans. Faraday Soc.*, 1929, **25**, 88.

¹¹ *Z. Elektrochemie*, 1933, **30**, 610.

X-RAY SPECTROGRAPHY OF POLYMERS AND IN PARTICULAR THOSE HAVING A RUBBER-LIKE EXTENSIBILITY.

By J. R. KATZ.

Received 13th August, 1935.

1. Introduction.

For many years H. Staudinger defended the theory that polymers have—in the simplest case—a long chain form of molecules in which a certain small unit repeats itself regularly along the chain, the units being united by primary valencies. His arguments were not, however, at the beginning of 1927, sufficiently convincing. The decisive argument was forthcoming shortly afterwards by the application of X-ray spectrography. I would like to begin this article by bringing a few personal memories about this development.

At the meeting of the *Naturforscherversammlung* in Innsbruck in September, 1924, I first heard him defend this theory, especially for the case of polyoxy-methylenes, but also for some other cases. Neither I myself nor some others to whom I spoke were convinced by his very interesting exposition. His conception seemed possible, but, many of us thought, not proved. And the whole subject did not yet look attractive to many of us.

At the meeting of the *Naturforscherversammlung* in Düsseldorf in September, 1926, where a symposium on high molecular weight substances was held, he again defended this theory. In 1926, the interest in the subject had already increased a good deal, as is clearly shown by the fact that a symposium on the subject had been arranged. Yet, Staudinger's conceptions did not seem to many of us really convincing, nor was the decisive value which X-ray spectrography could have for the subject yet understood at this meeting.¹ Under these circumstances there can be little doubt that the priority of the idea of the long chain molecules for polymers is chiefly due to H. Staudinger.

At the time this symposium in Düsseldorf was held (Sept. 1926) X-ray spectrography had not yet given the decisive argument as to the form of the molecules it would give later; it presented on the contrary a new difficulty in understanding them. H. Mark presented this situation, as it seemed at that moment, very clearly in his lecture for the Düsseldorf symposium.² All the X-ray data collected between 1920 and 1926 showed that the elementary cells of the crystals of all the high molecular weight substances then investigated (cellulose, stretched rubber, silk fibroin, etc.) are small, their weight not exceeding 800 times that of a hydrogen atom. Yet much physico-chemical and chemical evidence points to the fact that these substances, including highly polymerised synthetic polymers, have on the contrary a very high molecular weight,

¹ H. Staudinger, *Berichte*, 1926, **59**, 3019, containing his lecture at Düsseldorf.

² See the lecture of H. Mark, *Berichte*, 1926, **59**, 2982.

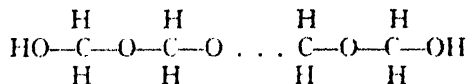
ranging in the tens or hundreds of thousands. It was still doubtful at the Düsseldorf meeting how this fundamental contradiction could be explained.

Some of us who worked on the X-ray spectrography of high molecular weight substances had discussed as one of the possibilities, the assumption that the molecules might perhaps be very much longer than the elementary cell of the crystals. M. Polanyi (1921) and R. O. Herzog (1921)³ early in the development of the X-ray spectrography of the high molecular weight substances discussed the *possibility* of such an assumption, without however deciding in its favour. I myself in 1924, in writing my first survey on X-ray spectrography of swelling, discussed the same hypothesis.⁴ And in 1925, in describing the X-ray phenomena obtained in stretching rubber, I even made this same assumption as the probable explanation.⁵ K. Weissenberg discussed the same possibility in 1925.⁶ Yet none of us worked this idea out completely for one substance.

In June, 1926, however, a young Californian botanist, O. L. Sponsler, made this next step.⁷ In the American Colloid Symposium, June, 1926, held at the Massachusetts Institute of Technology at Cambridge, Mass., he brought a complete picture of the cellulose molecule and how it lies in the elementary cell. He visualised the unit which repeats itself, the $C_6H_{10}O_5$, as a pyranose ring, the side chain $-CH_2OH$ being turned alternately to the left and the right, the unit being joined by primary valencies (glucosidic bindings) to a chain form molecule. This molecule is *very much longer* than the elementary cell. He described, using Bragg's sphere models, how the carbon and oxygen atoms lie in the elementary cell.

This was the first full picture which showed how to combine the assumption of the long chain molecule with the small elementary cell found by the X-ray workers and as such has now become a classic (although later Kurt H. Meyer and H. Mark had to make some changes in Sponsler's picture for cellulose, because they seemed more probable.⁸)

Then, in 1927 G. Mie and J. Hengstenberg,⁹ working in close collaboration with H. Staudinger made the decisive step. (Shortly afterwards, in 1928, Emil Ott, working also with H. Staudinger's substances, came in principle to the same conclusions.¹⁰) They found the following fundamental facts. The polyoxymethylenes, polymerisation products of formaldehyde, have according to the chemical investigations of H. Staudinger and his collaborators¹¹ the chemical structure :



³ M. Polanyi, *Naturwissenschaften*, 1921, **9**, 288 ; R. O. Herzog and W. Jancke, *Z. angew. chem.*, 1921, **34**, 385.

⁴ J. R. Katz, *Ergebn. exakt. Naturw.*, 1924, **3**, 363.

⁵ J. R. Katz, *Naturwissenschaften*, 1925, **13**, 1411 ; *Ergeb. exakt. Naturw.*, 1925, **4**, 169.

⁶ K. Weissenberg, *Z. Kristallographie*, 1925, **62**, 13 and 52 ; *Z. Physik*, 1925, **34**, 402, 406, 433.

⁷ O. L. Sponsler and W. H. Dore, *Colloid Symposium Monograph*, 1926, **4**, 174.

⁸ Kurt H. Meyer and H. Mark, *Berichte*, 1928, **61**, 593.

⁹ H. Staudinger, H. Johner, and R. Signer, G. Mie and J. Hengstenberg, *Z. physik. Chem.*, 1927, **126**, 425 ; H. Hengstenberg, *Ann. Physik.*, (4), 1927, **84**, 245.

¹⁰ Emil Ott, *Helv. chim. Acta*, 1928, **11**, 300 : see later also, *Science*, 1930, **71**, 465 ; *Z. physik. Chem.* 1930, **9B**, 378.

¹¹ H. Staudinger, H. Signer, H. Johner, M. Lüthy, W. Kern, D. Russidis and O. Schweitzer, *Ann. Chem.*, 1929, **474**, 145-275.

a chain form molecule ending on both sides in a hydroxyl group. These hydroxyl groups can either be acetylated or methylated and then can show, e.g. by determination of the number of acetyl groups the length of the chain. It proved to be possible to separate the different polymers from the mixture to such an extent that they seemed to be—on chemical analysis, as specified above—pure chemical substances.

On the other

hand, one can determine the length of the chain by X-ray investigations, and show that it increases proportionally to the number of CH_2O -groups, determined by the chemical method.

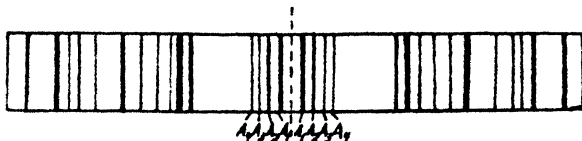


FIG. 1.

The main X-ray interferences of these different pure polymers are approximately the same, but there are a few central interferences which differ characteristically with the number of CH_2O -groups present in the polymer. The authors explained this characteristic fact by assuming that the interferences which are approximately the same in all the

polymers are given by the unit $\begin{array}{c} \text{H} \\ | \\ -\text{C}-\text{O}- \\ | \\ \text{H} \end{array}$ which repeats itself regularly along the chain form molecule. The variable interferences measure

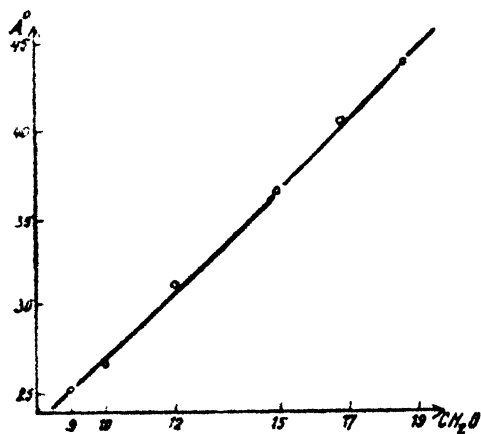


FIG. 2.

the length of the chain, they are the different orders of reflection of this length (or of a quantity directly related with it). Fig. 1 shows diagrammatically the X-ray pattern of a pure polyoxymethylene diacetate (at random distribution of the crystals). A_1 to A_4 are the first to fourth orders of reflection. The length of the molecule, as calculated from the A-interferences, is shown in Fig. 2. As it is a straight line, the length of the molecule as it lies in the crystalline lattice is proportional to the

number of CH_2O -units; therefore this molecule must have, in the crystal, approximately the form of a long straight rod. This X-ray result has to be considered as the first direct experimental evidence of Staudinger's hypothesis, and a decisive one. The length of one CH_2O -group was approximately 1.9 A.U.

These results were obtained with polymethylene diacetates, and with polymethylene dimethyl ethers. By pressing the material the crystals could sometimes be oriented parallel, and therefore fibre diagrams could be obtained; or the material had primarily the fibre form.

While in the case of the lower polymers (for instance, with 10 to 20 CH_2O -groups) the length of the molecule could be studied, this method failed in the case of the higher polymers. Here it was not possible to

separate the polymers into fractions having each one single chain length.¹² Such complex mixtures now showed a very interesting phenomenon. *The small interference rings related with the length of the molecule were failing.* This experience is especially interesting, as they have never been found in natural highpolymeric substances (like cellulose, rubber) and many synthetic polymers. So we are led to the assumption that in all such cases where these interference rings fail there are mixed crystals built up by molecules of such a different length that these interferences cannot be formed. Staudinger at once applied these results to cellulose, asserting that it had in principle the same structure.

The publications of Kurt H. Meyer and H. Mark in 1928—see paragraph 2—then brought a second experimental evidence for the hypothesis of a long chain molecule, this time of a more complicated nature. The authors worked out its meaning explicitly for cellulose, rubber, chitin and silk fibroin and made a very important contribution.

The spreading of some high polymeric substances (especially cellulose ethers) in a monomolecular film on a water surface, in films of reproducible thickness and only one hydrocarbon chain thick, which I was able to make in 1928 together with P. J. P. Samwel, may be considered as a third experimental argument for the long chain molecule. The homogeneity of the monomolecular films was doubted; but it was proved to exist in a number of cases by H. Zocher and F. Stiebel.¹³ Only their additional research made this experimental evidence fully convincing.

2. The Analysis of Crystalline Patterns of Synthetic Polymers.

A number of polymers can show a crystalline pattern; some others have only been found with an amorphous pattern. Some will only give a crystalline pattern when stretched, while they are amorphous in the unstretched form; this latter category we shall discuss later.

There is, however, in principle, no difference in the analysis of a fibre pattern in both cases.

Crystalline polymers are found, for instance, in the case of polyoxymethylenes, polyoxyethylenes, etc. Thiokol (polyethylene-tetra-sulphide), polychloroprene, polybromoprene, polyiodoprene can be found in the crystalline condition, but also in the amorphous state.¹⁴ Moreover, the polyesters, etc., of W. H. Carothers are often crystalline.

In all these cases, when we want to calculate the elementary cell of the crystal, we have to remember the following principles:

(a) When there is a random orientation of the crystals, it is in almost all cases impossible to derive any calculation about the elementary cell.

(b) When we can get all the crystals exactly parallelised, and when they have a sharp lattice, we can get a good fibre pattern. The parallelism can be effected either by stretching or by pressure; in both cases a somewhat plastic condition may be advantageous, or an elastic one in other cases.

¹² See, however, Emil Ott, *Z. physik. Chem.* 1930, **9B**, 378, who studied long chain polymers in which all the molecules seemed to have the same length. In a "paraformaldehyde," e.g., he found a chain length of 60.6 Å.U., for a γ -polymethylene oxide one of 113 Å.U.

¹³ J. R. Katz and P. J. P. Samwel, *Naturwiss.*, 1928, **16**, 592; *Ann. Chem.*, 1929, **472**, 241; H. Zocher and F. Stiebel, *Z. physik. Chem.*, 1930, **147A**, 401; N. K. Adam, *Trans. Faraday Soc.*, 1932, **29**, 90.

¹⁴ Thiokol, polychloroprene, polybromoprene can either crystallise spontaneously or become crystallised by stretching. The two kinds of crystals are not necessarily always the same.

(c) In special cases, for instance when stretching very thin films, we may get a higher degree of orientation of the crystals; for instance, not only is a fibre diagram found when such a stretched film is investigated with a primary beam of monochromatic X-rays, perpendicular to the surface of the film, but another regular arrangement will be found when investigated parallel to the surface of the film.

In the case mentioned under (c) there is a higher degree of probability of finding the real elementary cell than in case (b). I have analysed these facts in my book, *Die Röntgenspektrographie als Untersuchungsmethode bei hochmolekularen Substanzen, bei Kolloiden und bei tierischen und pflanzlichen Geweben*.^{14a} It seems unnecessary to give here more than a short outline of the discussion given there. Really certain results can only be obtained with macroscopic single crystals; and those cannot be prepared—it seems now—in the case of most substances of a very high molecular weight.¹⁵

In the cases mentioned under (b) and (c) *it is not possible with real certainty to calculate the elementary cell of the crystal; the only thing we can calculate with full certainty is the period of identity in the fibre axis; but the two axes perpendicular to the fibre axis and the angle between them cannot be calculated with real certainty from a fibre diagram* (even in case (c)). If one investigates, however, for many years one single substance (as R. O. Herzog's school did with cellulose) one can come to a good approximate degree of certainty in the solution one has found. One must be sure to have found *all* the interferences (including the very weak ones) which can be made visible; one must be certain that they are not due to secondary factors, etc.

The uncertainty of this kind of results in other cases, can be best shown by a practical example. H. Mark—certainly one of the best workers in the field—has calculated together with G. von Susich the elementary cell of stretched rubber from the fibre diagram using thin films (see under (c)). He found that the lattice has place for seven isoprene groups, while the number ought to have been eight. In order to reconcile this contradiction, the authors have to assume that pure rubber has a specific weight 10-15 per cent. larger than actually found.¹⁶ All my rubber friends agree with me that such a high specific weight for racked rubber is extremely improbable.

I would, therefore, advise young investigators to be very reticent in undertaking such determinations—unless they are content to get only a *probable* solution of the problem and in their publication explicitly state so—and not to publish until they have studied many fibre diagrams of their substance made under different circumstances.

The elementary cell once "found" we can proceed to the location of the molecules in it, if the structural formula of the organic compound is sufficiently known. This is a still more delicate procedure than the calculation of the elementary cell. It requires a thorough knowledge of crystallography of organic substances to make a good guess, and often—I am sorry to say—is done without an approximate comparison of the relative intensities of the interferences.

In this way we can only come to a probable solution of the problem and no more. If this is duly emphasised in the publication, nothing is

^{14a} Berlin and Wien, 1934. Urban and Schwarzenberg.

¹⁵ Compare, however, the large oxyhemoglobin crystals made by M. Arthus and others (7 mm. and over more), e.g. by alcohol dialysis of a solution in water.

¹⁶ H. Mark and G. von Susich, *Koll. Z.*, 1928, 36, 11.

to be said against this procedure. But if it is insufficiently emphasised—as nowadays not rarely happens—then it has the danger of making outsiders give much more credit to these results than they deserve. In this way we are in danger of coming to a construction of results which are not well-grounded and yet materially influence our trend of thought.

On the other hand, it ought to be emphasised that the basic work of this kind on cellulose, rubber, chitin of Kurt H. Meyer and H. Mark¹⁷ in 1928, and the one on polymethylene diacetate, etc., has been an important service to science.

It must not be forgotten that this work of Meyer and Mark has very much contributed to the present day general acceptance of the conception of the long chain molecules, and that it brought to light many other new points of view. These researches have shown us what form the molecules of some of the most important high polymeric substances very probably have and how they probably lie in the elementary cells. Especially in teaching the subject, there is a great advantage compared with the situation ten years ago. We then had to tell our students that we did not understand very much about the structure of these substances. That was very discouraging. Now we can tell them, "look here, *this* is the probable form of the molecule and *this* is their probable place in the crystalline lattice; may be all this is not perfectly certain but it is at least a very good first approximation to the truth, an example how things might be." Where the work so relied on is based on pretty solid ground this is a great advantage in teaching. And not only in teaching but in many other cases where application of this picture of the facts proves useful in colloid chemistry or in industry. It gives us at least a first approximative picture of the truth.

3. Results of X-ray Analysis of Crystalline Synthetic Polymerisates.

Except for the polyoxymethylene derivatives where Mie-Hengstenberg⁹ and Emil Ott¹⁰ got about the same but slightly divergent results, only a few substances in the group of synthetic polymers have been sufficiently investigated. Here a large field for further investigation lies open. I would draw attention to some interesting conclusions drawn by Edwin Sauter out of the X-ray analysis of polyethylene and polymethylene-oxides.¹⁸

Especially promising, I believe, is the group of the polyesters synthesised by W. H. Carothers and collaborators, as, e.g., the polyester of sebacic acid and ethylene glycol. As we can systematically vary both the number of carbon atoms of the dibasic acid and of the dialcohol, we could get a homologous series of polyesters. Here the calculation of the two axes perpendicular to the fibre axis would lead to the possibility of a check on the figures got for each of the individual polyesters, by comparison. (Polymorphism would have to be carefully taken into consideration as a possible complication.) Then the results calculated for, let us say, ten or fifteen different polyesters would be far less uncertain than the result calculated for one single term of the series.

The same could be done for analogous substances synthesised by

¹⁷ Kurt H. Meyer and H. Mark, *Ber.*, 1928, 61; for cellulose p. 593; for rubber, p. 1939; for chitin, p. 1928.

¹⁸ Edwin Sauter, *Z. physik. Chem.*, 1933, 21B, 161 and 186.

Carothers, Hill and collaborators, such as polydibasic acid anhydrides, polyamino acids, etc.

This would be a lengthy piece of work, but it might help us, perhaps more than anything else, to understand better than we do now, how much value has to be given to the calculations of the elementary cell and the position of the molecules in it now made more and more for different high molecular weight substances.

4. The Analysis of Amorphous Patterns of Synthetic Polymers.

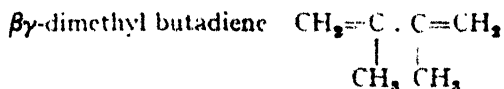
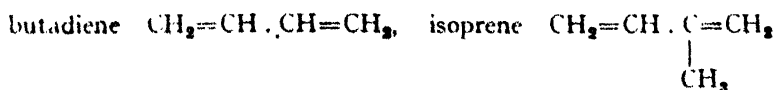
Here the uncertainty of the conclusions is much greater than in the case of crystalline fibre diagrams. But as in that case, an approximate picture of the truth may be gained, if care and discretion is used in applying the method of analysis.

The analysis of the amorphous polymers seems especially interesting in the case of rubber and other substances which "crystallise" on stretching. We shall come back to this question in paragraphs 6 and 7. The "amorphous unstretched rubber" must contain in its "amorphous" structure in some way (at present not understood) a preformation of the highly parallelised and three-dimensionally ordered structure in which the molecules lie when the rubber has been stretched.

This is the reason why I undertook in 1926 the study of the amorphous patterns of rubber and polymers and compared them with the X-ray patterns of about 400 organic liquids. I hoped by the comparison of both groups of patterns to find a method of approach for the study of amorphous polymerisates.

Unhappily the results of this research have not yet been duly published. A review of the work done on a part of the large number of organic liquids was published in Dutch in J. Selman's doctor's thesis (Amsterdam, 1932). A short review of our work on organic liquids—in an initial state of the work—was published at the beginning of 1928.¹⁹ Many of the results published there were arrived at independently of G. W. Stewart and of C. V. Raman's pupils. On the other hand, their work corroborates and enlarges our collection of X-ray negatives kept for the analysis of amorphous polymers. We came independently to the same conclusion, that the molecules in a liquid lie in parallel groups—each molecule changing constantly from one group to the other—while the axes of these groups lie distributed at random, and that the average form of the molecule is more rigid than was formerly assumed.

As a matter of fact, I have about 400 X-ray patterns of well-chosen organic liquids to compare with the pattern of the polymers; and this comparison often leads to an analysis of the pattern of the polymer. As a simple example of this kind of analysis, let me give an analysis of the four typical types of polymers described by Harries in 1912 in his classical researches on the polymerisation of butadiene, isoprene, and dimethyl-butadiene. Butadiene, isoprene, dimethylbutadiene have, as is known, the structural formulæ:



¹⁹ J. R. Katz, *Z. angew. Chemie*, 1928, 41, 327.

These three liquids give X-ray patterns of the same type; the chief amorphous ring having a period of identity, calculated according to the Bragg formula, of

Butadiene	4.6 Å.U.
Isoprene	4.9 Å.U.
Dimethylbutadiene	5.3 Å.U.

Consulting the patterns of the other organic liquids, we can explain what these numbers mean. The distance, 4.65 Å.U., is the distance we always find for a liquid having straight, not ramified carbon chains as molecules, if this chain is 4 carbon atoms long or longer (however long it may be). It is the same for hydrocarbons, ketones, alcohols, acids, mercaptans (the other group being attached to one end of the hydrocarbon chain). In the picture to which Stewart, Raman's pupils and I have come, this means that in all these liquids the molecules lie in little groups of parallel molecules, the distance of these parallel molecules in the direction perpendicular to the parallelism being just 4.65 Å.U.

Now, if the hydrocarbon or alcohol—having a straight chain of at least four hydrocarbons—has one or two methyl groups as side chains, what do we find? *Just such an increase in distance as we have found for the butadienes*: 0.3-0.4 Å.U. for one methyl group, 0.6-0.7 Å.U. for two methyl groups. In the picture of a liquid to which both Stewart, Raman's pupils and I have come, this means that the increased distance between parallel hydrocarbon chains in the small groups is 0.3-0.4 Å.U. larger for one methyl group, 0.6-0.7 for two.

In this picture, the amorphous patterns of the three liquid butadienes are easily understandable.

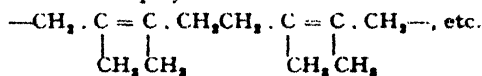
Now, if these substances polymerise on being heated, what changes happen in their molecules? According to Staudinger, the following substances are formed:

Butadiene thermal polymer— $\text{CH}_2 \cdot \text{CH}=\text{CH} \cdot \text{CH}_2\text{CH}_2-\text{CH}=\text{CH} \cdot \text{CH}_2-$, etc.

Isoprene thermal polymer— $\text{CH}_2 \cdot \text{CH}=\text{C} \cdot \text{CH}_2\text{CH}_2 \cdot \text{CH}=\text{C} \cdot \text{CH}_2-$, etc.

$\begin{array}{c} \text{CH}_3 \qquad \qquad \qquad \text{CH}_3 \\ | \qquad \qquad \qquad | \end{array}$

Dimethylbutadiene thermal polymer:



*What kind of amorphous patterns have these thermal polymers? Practically the same patterns as the liquids from which they were polymerised.*²⁰ For the period of identity of the chief ring calculated according to the Bragg formula, we found:

Butadiene thermal polymer	4.6 Å.U.
Isoprene	"	"	.	.	.	4.9 "
Dimethylbutadiene	"	"	.	.	.	5.3 "

An astonishing fact, that these low boiling liquid butadienes almost have the same amorphous pattern as the thermal polymers made from them! But this is just the consequence of the Staudinger formulæ; just what one would have to expect on the basis of these formulæ. Remember, the distance between the molecules in the groups (perpendicular to the chief chain) is

²⁰ J. R. Katz, *Z. physik. Chem.*, 1927, 125, 321; J. R. Katz, J. Selman and Lottelise Heyne, *Z. Kautschuk*, 1927, 214.

independent of the length of the chief chain, if this is at least four carbon atoms long.

Now, if we make the three other polymers described by Harries in 1912, what do we find? Harries distinguished the following three polymers:

(a) What we now call the *Kondakow-polymer* (which grows slowly in the liquid in a form resembling a cauliflower, at room temperature).

(b) The *sodium polymerisate*, made by the interaction of metallic sodium on the liquid butadiene.

(c) The *sodium-carbonic-acid polymerisate*, made by the introduction of metallic sodium in a liquid saturated with carbonic acid.

It was found by him and often corroborated by others that (b) and (c) are very different substances; their ozonides, for instance, split with warm water into very different substances. On the contrary, (a), (c) and the thermal polymerisate show a good deal of analogy with one another.

Now, what does X-ray spectrography show? That the Kondakow and the sodium-carbonic-acid polymers have practically the same amorphous X-ray pattern as the thermal polymers, *while the sodium polymers have a totally different amorphous pattern, very different from the liquid patterns*. This corresponds pretty well with the different splitting up of the ozonides of the sodium polymers observed by Harries and with a number of facts described in later years. The X-ray patterns of the sodium polymers seems to show—by comparison with the patterns of certain organic liquids—that the chief straight carbon chain carries a large number of carbon chains which must be longer than one carbon atom. Some facts from organic chemistry seem to point in the same direction.

In the same way the phenol-formaldehyde polymers might be analysed by comparison with the liquid patterns of the phenols, especially if the side chains of the phenols are systematically varied. R. Houwink has already begun to make an investigation of this kind.²¹ Here, as Kurt H. Meyer and H. Mark first emphasised, the molecule might have the form of a large flat disc.

The more I have had the opportunity to study amorphous polymers of different kinds, either from a scientific or from a technical point of view, the more I have found the comparison with the patterns of a large number of organic liquids a fruitful method. In the course of years one learns to build out one's collection of organic liquids in the direction in which one wants it.²² And generally one is able on this basis to give an interpretation of the amorphous pattern of the polymer.

²¹ R. Houwink. *Physik. Eigensch. u. Feinbau. v. Natur- u. Kunstharzen*, Leipzig, 1934.

²² In recent years B. E. Warren has developed a somewhat different method of analysis of liquid patterns than Stewart, Raman's pupils and I have used. The pattern taken up *in vacuo* with purely monochromatic light is analysed by the photometer and the intensity curve analysed by Fourier analysis. An application of this method to the analysis of the amorphous pattern of rubber has just been announced (see *Physical Review*, 1935, 47, 808), but not yet published at sufficient length to compare it with our conception. It shows in principle three periods of identity to exist in the rubber, the period of 4.9 Å. mentioned above is interpreted as the shortest distance of a carbon atom from the next carbon atom of an adjacent chain, the two others as intramolecular periods of identity (of a carbon atom to the next, on to the next but one carbon atom of the chain). Warren's method is, I believe, a very promising one.

5. Amorphous Patterns of Synthetic Polymers.

In the case of a number of polymerisations the amorphous pattern of the polymer is not simply the same as in the non-polymerised liquid. It can be different, according to our observations in the year 1927, and in two different ways.²³

(1) Either it is entirely different—as already described for the sodium polymers of the butadienes; this behaviour is found in polymerisation of vinyl acetate to polyvinyl acetate, or of methyl acrylate to polymethyl acrylate; or

(2) All the interferences of the liquid are found again in the amorphous pattern of the polymer, but one ring of small diameter is added, which I have called the *polymerisation ring*. This behaviour is found in styrene-polystyrene; cumarone, polycumarone; indene, polyindene. Liquid styrene, for instance, has an amorphous ring $d = 4.85$ Å.U., metastyrene the same ring $d = 4.85$; but, in addition, a small ring $d = 10.0$ Å.U. (Figs. 3 and 4). Just so liquid indene has an amorphous ring $d = 5.15$ Å.U., while polyindene has the same ring, but in addition a small ring $d = 10.1$ Å.U.

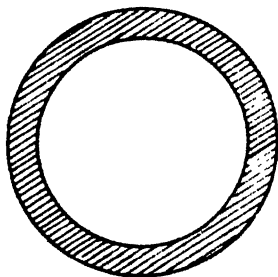


FIG. 3.—Styrene.

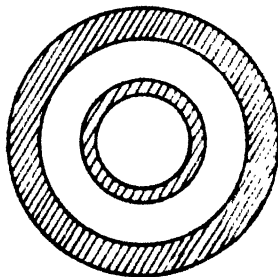
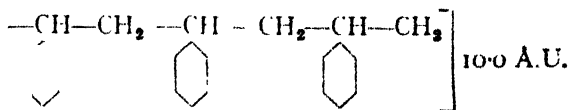


FIG. 4.—Polystyrene.

It has been difficult, for a long time, to understand the meaning of this polymerisation ring. In the case of polystyrene, however, it has been cleared up a good deal in the course of the last year by the fact that C. S. Fuller and I were able—by stretching polystyrene without making it crystalline—to split the polymerisation ring into two equatorial maxima.²⁴ This seems to indicate, as in the case of the splitting of the mesomorphic ring of *p*-azoxyanisole in a magnetic field, that the long molecules are oriented by the stretching, with their longest direction in the direction of the stretch. According to Staudinger polystyrene must have the formula



The distance between two parallel chains might easily be 10.0 Å.U.

²³ J. R. Katz, J. Selman and Lottelise Heyne, *Z. Kautschuk*, 1927, 217; *Z. physik. Chem.*, 1927, 125, 321.

²⁴ Probably Miss M. Hühnemörder, *Z. Kautschuk*, 1927, 106 and 126 has made the same observations as we. But I am not sure that her patterns do not show a change through stretching which goes further than ours, perhaps incipient crystallisation.

In the liquid benzene derivatives the flat benzene rings probably lie like a roll of coins on one another; we must assume, as all the interferences of the liquid styrene are found again practically unchanged in the polystyrene, that the flat benzene rings lie very much in the same way in the amorphous polymerisation product. But because of the polymerisation a new period of identity is found, which we have tried to explain in the above-mentioned way.

A very interesting change of the amorphous patterns through stretching is observed when stretching certain samples of polyvinyl acetate. At room temperature they are resinous, at 100° C. the substance is elastic like a piece of rubber. When stretched the substance does not "crystallise," but the inner one of the two amorphous rings develops two equatorial intensity maxima (Fig. 5). This inner ring has a $d = 7.05$ Å.U. According to the theory of Staudinger the formula of polyvinyl acetate is probably

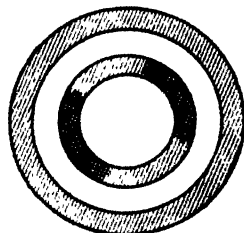
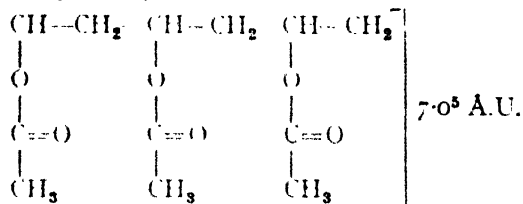


FIG. 5.



As the inner ring develops two equatorial maxima of intensity on stretching, probably the chief chains orient themselves parallel to the direction of the stretch. The distance 7.05 may correspond to the distance between the two parallel hydrocarbon chains. The outer ring $d = 4.05$ Å.U. is more difficult to explain—perhaps it is the distance between adjacent acetyl side chains.

Queerly enough, many polymers, for instance, isoprene thermal polymer, polymethyl acrylate, etc., do not show any change in their X-ray pattern, an amorphous one, when they are stretched. Such substances should, however, once stretched, be cooled down at once in liquid air and be investigated at its temperature. The relaxation then would be prevented, and one may perhaps observe a change in X-ray pattern which now escapes us.

6. "Crystallisation" of Amorphous Rubber when Stretched as a Comparison for Synthetic Substances which Behave in an Analogous Way.

Before describing the X-ray phenomena observed when synthetic polymers with a rubber-like elasticity are stretched, it is necessary to describe shortly the X-ray phenomena which have been observed in the stretching of natural rubber. In these synthetic substances frequently the "crystallisation" phenomena are not so fully developed; they are more rudimentary than in the natural substance. We shall in the next paragraph try to indicate how and why.

In 1924, while playing with an ordinary rubber band, I accidentally observed that it was transparent when unstretched and regularly became opaque when stretched. I made a wild guess: something unmixed and

becomes opaque like a phenol-water mixture which is cooled off. So I made an X-ray experiment and really found that a new "phase," in the sense of the phase rule, was formed by stretching the rubber. *This phase is a "crystalline" one* and all the little "crystals" are parallel (with the same crystallographical axis) to the direction of stretch. The X-ray pattern of the unstretched rubber was "amorphous," while that of the stretched rubber was a "crystalline" fibre pattern,—superimposed over a weakened amorphous ring.

The fibre pattern shows, moreover, that the rubber must have acquired a fibre structure by being stretched. And that this was the case was also shown by L. Hock by freezing the rubber in liquid air and then hammering it; the fissures will all lie in the direction of the stretch, while in unstretched rubber they will lie distributed at random.^{24a}

In stretching the rubber I found there was a *critical stretch* (about 80 per cent. elongation for unvulcanised rubber). A smaller elongation will never produce any "crystalline" interferences; above this critical elongation the intensity of interferences will be the greater the larger the

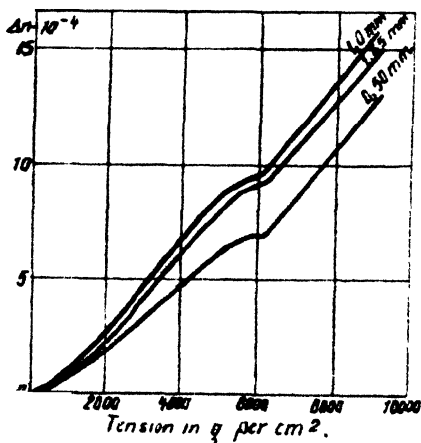


FIG. 6.

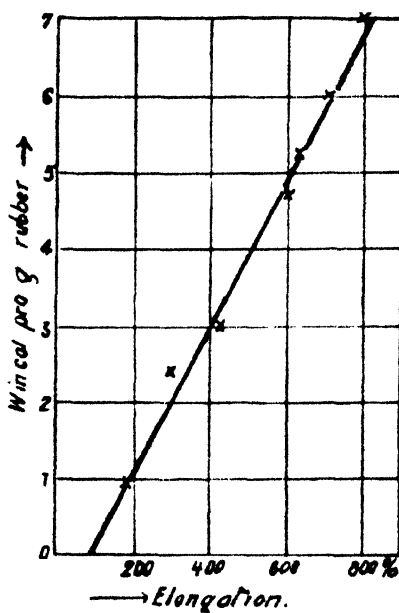


FIG. 7.

elongation. In these elongations below 80 per cent. the rubber molecules get already oriented in the direction of the stress; but they do not yet "crystallise": arrange themselves into a three-dimensional lattice.

This "crystallisation" I concluded must be the chief component of the Joule heat of rubber, the heat developed by rubber when stretched (as every transition of amorphous to crystalline must give a good deal of heat).

These X-ray phenomena of stretched rubber I first described and developed in two journals which are not much read in England and America.²⁵ My experiments were soon confirmed and further developed by other authors.²⁶

^{24a} L. Hock, *Z. Elektrochemie*, 1925, 404; *Z. Kautschuk*, Oct., 1925.

²⁵ *Naturwissenschaften*, 1925, 13, 411; and *Gummi-Zeitung*, 1927, 41, Nos. 36 and 37.

²⁶ E. A. Hauser and H. Mark, *Kolloidchem. Beihefte*, 1926, 22, 88; G. L. Clark, *J. Ind. Eng. Chem.*, 1926, 18, 1131.

The arrangement and parallelisation of the rubber molecules below the critical elongation was investigated at my instigation by W. C. van Geel and Miss J. G. Eymers.²⁷ Below the critical elongation the optical anisotropy depends (through an S form curve) on the elongation; then there is a sharp break, a real discontinuity in the curve: and above the critical elongation the optical anisotropy is strictly proportional to further increase in elongation (Fig. 6).

The heat developed through the "crystallisation" is zero till the critical elongation is reached. Then it is strictly proportional to the further increase in the elongation (L. Hock and S. Boström).²⁸ (Fig. 7). The intensity of the "crystalline" interferences depends in the same linear way on "the amount of elongation above the critical point" (E. A. Hauser and H. Mark).²⁹

7. Rubber-like Synthetical Substances which "Crystallise" when Stretched.

(a) Polyvinyl Alcohol.

Several amorphous polymers have been studied lately which give a good fibre diagram on being stretched. *Polyvinyl-alcohol* in a certain state of polymerisation at a certain temperature was described as giving a perfectly sharp fibre diagram when stretched (F. Halle). A picture of the fibre diagram is given, but further details are lacking in the preliminary publication.³⁰ It would be especially valuable to know if there is a sharp critical elongation, and if curves Figs. 6 and 7 are the same for polyvinyl-alcohol as for rubber.

(b) Polyethylene Tetrasulphide (thiokol).

C. S. Fuller and I studied recently³¹ the X-ray pattern of *polyethylene tetrasulphide (thiokol)*. From the as yet unpublished article I may quote the following facts. It is generally found "frozen," that is to say, crystalline; it is then hard, brittle, inelastic. When heated above 70° C. it melts, and then becomes an elastic rubber-like substance, used in industry because it is a rubber-like body which is resistant against oil and organic solvents. It is made by interaction of $\text{ClCH}_2 \cdot \text{CH}_2\text{Cl}$ with Na_2S_4 , and forms a polymer (much in the same way as Carother's polyesters) having the empirical composition $[\text{CH}_2 \cdot \text{CH}_2\text{S}_4]_n$, where n is a very large number.

In the frozen condition it has a crystalline pattern; in the unstretched rubber-like form it has an amorphous pattern consisting of two amorphous rings ($d_1 = 10 \text{ \AA.U.}$, $d_2 = 4.65 \text{ \AA.U.}$).

When stretched, the substance behaves like rubber. It then gives a beautiful crystalline fibre pattern, having very sharp interference spots. The period of identity b in the direction of the fibre axis is 4.32 \AA.U. , or probably double this. Treated with a 10 per cent. sodium sulphate solution, one half of its sulphur is taken away. It then has the composition $[\text{CH}_2\text{CH}_2\text{S}_2]$; this has a period of identity in the fibre axis twice as

²⁷ W. C. van Geel and J. C. Eymers, *Z. physik. Chem.*, 1929, B3, 240.

²⁸ S. Boström, *Kolloidchem. Beihefte*, 1928, 26, 439.

²⁹ E. A. Hauser and H. Mark, *loc. cit.*

³⁰ Fr. Halle, *Kolloid. Z.*, Dec., 1934.

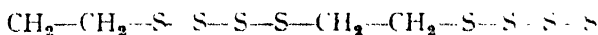
³¹ During my stay as a Baker non-resident lecturer in Cornell University in the first term of 1934-1935.

large. We tried to calculate the elementary cell and found as a possible solution a monoclinic space lattice

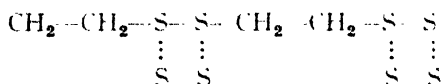
$$\begin{aligned}a &= 8.68 \text{ \AA.U.} \\b &= 8.64 \text{ \AA.U.}, \text{ or } 4.32 \text{ \AA.U.} \\c &= 5.03 \text{ \AA.U.} \\\beta &= 87^\circ,\end{aligned}$$

in which two, or one group $\text{C}_2\text{H}_4\text{S}_4$ is present per unit cell; these figures have to be taken with all the reserve mentioned in paragraph 2. The unit cell probably has the larger size and contains two $\text{C}_2\text{H}_4\text{S}_4$ units; but no interferences have so far been found in the tetrasulphide, forcing us to make this assumption.

Important evidence can, however, be drawn from the value 4.32 \AA.U. , found for the period of identity in the fibre axis. Two formulae seem possible for the polytetrasulphide. Either it is



or



The X-ray pattern forces us to give up the first formula and to accept the second; the unit of the first is far too long to fit in the dimension 4.32 \AA.U. , while $\text{CH}_2-\text{CH}_2-\text{S}-\text{S}$ just fits in well. The two other sulphurs must then be loosely attached, not forming a part of the chief valency chain. This corresponds very well with Patrick's observation, that one half of the sulphur can be easily taken away as by a 10 per cent. sulphite solution. This disulphide has a period of identity in the direction of the fibre twice as great as the tetrasulphide.

In the polyethylenesulphide series we have again the same advantage as in the polyester series mentioned in paragraph 3. Instead of ethylene, Patrick has furnished us with methylene or propylene, giving polymethylene-tetra-sulphide or polypropylene tetrasulphide. If our lattice is well calculated, there ought to be logical changes when comparing these substances. The sulphur content can, moreover, be made larger or smaller, oxygen can be added, etc., so a good check on the lattices calculated is possible.

We are now working on this programme. Determinations of the critical elongation, or like Figs. 6 and 7, have not yet been made, but will be made soon.

(c) Polychloroprene (Du Prene) and Polybromoprene.

Kenney³² has found that these substances are amorphous in the unstretched condition, while they have a crystalline fibre diagram superimposed over a weakened amorphous ring when it is stretched. The period of identity in the fibre axis is 4.9 \AA.U. , showing that we have to do with a *trans*-form like gutta-percha hydrocarbon and not with a *cis*-form like rubber hydrocarbon (the unit would then have an approximate length of 4.1 \AA.U.).³³ *Polychloroprene therefore is a derivative of gutta-percha hydrocarbon and not of rubber.*³² The fibre pattern has a characteristic property: while the equatorial interferences are very sharp, the layer

³² See W. H. Carothers, I. Williams and J. S. Kirby, *J. Amer. Chem. Soc.*, 1931, **53**, 4203-25.

³³ According to the conception of Kurt H. Meyer and H. Mark.

line interferences have a varying degree of unsharpness; there is probably some further complication in the problem than we have stated above. I have made many X-ray pictures of these substances and can corroborate these observations and conclusions out of my own experience. I hope soon to come back to these substances in an explicit publication.

(d) Methyl Rubber (*thermal polymer of $\beta\gamma$ dimethylbutadiene*).

This substance gives—as we have shown in 1927³⁴—a fibre diagram on stretching; but this diagram was not fully developed. The sharpness of the fibre pattern depends on the sample of methyl rubber investigated. L. Hock using another sample did not find any crystallisation on stretching when he worked at room temperature, but only when he cooled the sample.³⁵

(e) Isoprene Rubbers.

Isoprene rubbers have never given, so far, any sign of crystallisation when stretched, not even a change in their amorphous rings. Perhaps, however, they ought to be investigated at low temperature, or better be cooled immediately after they have been stretched.

(f) The Synthesis of Rubber out of Isoprene has not yet been made.

As no isoprene rubber has so far given any sign of crystallisation when being stretched; as this "crystallisation" on stretching is one of the most characteristic qualities of rubber, I still maintain—as I did in 1920—that *the synthesis of natural rubber has not yet been achieved*.³⁶ Synthetic isoprene rubber is yet a different substance from natural rubber. Steinmig was probably right in 1912 when he predicted that natural rubber would never be synthesised, because we cannot achieve a regular sequence of the methyl groups in the synthetic product. In polychloroprene and polybromoprene the activity of the molecules due to the Cl or Br may make this regular attachment more easy. But is the lack of sharpness of the layerlines due to the cause as Steinmig indicated, but working to a minor degree? Or to alternations of *cis* and *trans* units? Butadiene rubbers will always be found in forms which crystallise on stretching as their molecules have no side chains.

(g) Synthesis of Rubber ought to be done under X-ray Check.

As the "crystallisation" on stretching is a typical quality of any good rubber-like material the synthesis ought to be worked out so that the material gets a better and sharper fibre pattern on stretch.

Especially for the industrial production of butadiene rubber this may prove, I think, an important method for the improvement of existing types of synthetic rubber. As conditions are forcing more and more countries (e.g. Russia, Germany) to prepare a part of the rubber they need synthetically, this point of view seems to me to be again of considerable materiality.

"Crystallisation" of rubber or rubber-like substances on stretching is such an extremely characteristic property of them, that where it is

³⁴ J. R. Katz and P. van Campen, *Chem. Z.*, 1927, **51**, 53. Good pictures of these X-ray patterns in my book, *Die Röntgenspektrographie als Untersuchungsmethode bei hochmolekularen Substanzen*, etc. p. 150.

³⁵ *Z. physik. Chemie*, 1928, **134**, 271.

³⁶ J. R. Katz, *Ist die Synthese der Kautschuks schon gelungen? Ambonn-Festschrift* (Koll. Beih.), 1920, 341.

defective something essential is lacking in the molecular structure of the rubber (see the next paragraph, however).

8. Spontaneous Crystallisation of Natural Rubber and of Synthetic Polymerisates ; their Melting-Point.

In addition to the "crystallisation" on stretching, both natural rubber and some of the synthetic substances with a rubber-like extensibility show another form of crystallisation, this time a real and spontaneous one. When kept at a well-chosen low temperature—different for each substance—its amorphous pattern is changed into a crystalline pattern. At the same time it loses its transparency, becomes hard and inelastic ; it ceases to have a rubber-like extensibility. If the amorphous substance is cooled down too far (e.g., in liquid air), it will not crystallise, evidently because the velocity of crystallisation has been too much reduced. When the once crystallised substance is heated, it often has a pretty sharp melting-point.

In two cases—natural rubber and thiokol—it has been shown that the melting interval is quite short. Samples were kept for some time (e.g., a day) in thermostats at constant temperature, then examined shortly afterwards, both with X-ray spectrography and for specific weight, hardness and transparency. They were found to have a fairly sharp melting-point, the melting interval being in both cases only a few degrees.³⁷

In the case of natural rubber the melting-point seems to vary with the age of the crystalline rubber ; in the case of thiokol this was not found. In old natural rubber it lies at about 36° C., in thiokol at about 70° C.

In natural rubber the interesting fact was found that the X-ray pattern found by the spontaneous crystallisation shewed the same lattice as the one formed by stretching. This fact makes it difficult to understand why the crystalline pattern once formed by stretching disappears again when the stretched rubber is relaxed.

9. Explanation of the X-Ray Phenomena of Rubber and of Rubber-like Substances.

The following facts have also to be taken into account, before considering an explanation as valid :—

(a) The Substances which show a Rubber-like Extensibility.

The organic substances which show rubber-like extensibility seem all to have a long chain molecule. They are :

α. Organic polymerisation made of unsaturated compounds : Butadiene rubbers, polychloroprene, polybromoprene ; metastyrene ; polymeric methyl or ethyl ester of acrylic acid ; polymeric vinylacetate ; and polyvinyl alcohol.

β. Certain swollen proteins : Gelatin swollen in water, or in water-alcohol, or in water-glycerin ; silk fibroin swollen in formic acid ; collagen swollen in certain swelling agents ; α -keratin, swollen in water, especially after stretching and relaxation.

γ. Perhaps, cellulose, swollen in sodium hydroxide solutions, and certain cellulose derivatives swollen in organic compounds.

³⁷ For rubber, see J. R. Katz and K. Bing, *Z. angew. Chem.*, 1925, 38, 439 ; A. van Rossem and J. Lotichius, *Z. Kautschuk*, 1929, 5, 2 ; J. R. Katz, *ibid.*, p. 8. For thiokol see J. R. Katz and M. T. Bush (*not yet published*).

Moreover, there are some *inorganic* rubber-like substances, *e.g.*, *sulphur* and *polymerisation products of $PNCl_2$* ; probably these inorganic substances also have a long chain molecule.

(b) All these Rubber-like Substances have some Typical Characteristics.

- α . They develop heat when stretched (like the Joule heat of rubber).
- β . They show fibre structure when stretched and frozen in liquid air; the fissures on mechanical treatment all run parallel to the direction of the stretch.
- γ . They show, especially when they "crystallise" on stretching, a characteristic stress-strain curve comparable with that of natural rubber.
- δ . They show optical anisotropy when stretched, depending in characteristic curves on the degree of stretching.

(c) In all these Substances the Rubber-like State only Exists Within a more or less Narrow Range of Temperatures; Swelling Reduces these Temperatures.

The upper temperature is the one where the elastic substance becomes plastic; it is not generally sharp. The lower limit—called in 1915 by Ostromyslen-ski the "dead temperature"—is the temperature where the rubber changes into a resin. It is accompanied—as Martin Ruhemann and F. Simon have shown—³⁸ by a large drop in the value of the specific heat; this drop is analogous to the drop in specific heat when liquid glycerin is changed by cooling into a glass. The "dead temperature" again is a temperature interval which, however, may be quite short (*e.g.* 10°).

If a liquid which swells the rubber-like substance is added, the "dead temperature" is decreased even to a large extent. The *elasticators* of Hofmann (dimethylaniline, dibenzyl ether, etc.) were well known to have this effect in the case of methyl rubber (heat polymerisate of *β*-dimethylbutadiene). As a matter of fact the methyl rubber acquired a sufficient elasticity only after the addition of an elasticator. That gelatin, silk fibroin, etc., acquire rubber-like elasticity only after being strongly swollen is again an "elasticator effect," but a very much stronger one than in the case of methyl rubber.

(d) In the Case of Natural Rubber, the Discontinuity in the Curve of the Optical Anisotropy as a Function of the Elongation shows that there are Two Phases in the Stretching of Rubber.

In the first phase the molecules are oriented into the direction of the stretch and perhaps stretched; but they do not yet form a three-dimensional arrangement. In this part of the curve the optical anisotropy increases according to an S-form curve (as in a nematic phase when its molecules are oriented parallel by a magnetic field); see Fig. 6.

The critical elongation is the stretch, where the initially parallel molecules are forced into a three-dimensional arrangement. As the stretch increases, more and more bundles of molecules are forced into this three-dimensional arrangement, *i.e.*, are forced to reach their critical value.

This formation of crystals may have to do with the characteristic form of the stress-strain curve of rubber, specially with the fact that the

³⁸ Martin Ruhemann und F. Simon, *Z. physik. Chem.*, 1928, **128**, 1.

elasticity at a certain stretch is almost exhausted. Mallock explained this fact long ago in connection with the resistance of putty to stretching. When the oil film between the chalk particles gets too thin, the putty is not stretched so easily as at first, "it stiffens up."

(e) Conclusions.

All these facts have to be explained before we can accept a theory for the rubber-like elastic extensibility as valid. There are two conceptions possible, *either* we consider the rubber molecule itself as the structure which is stretched and retracts; stretching then converts the coiled-up molecule into a straight one, *or* we assume that the structure which gives the rubber-like extensibility is larger than a molecule.

As the second hypothesis could not be worked out in a good form, one has turned more and more to the first. It would serve to explain the X-ray phenomena on stretching of rubber, and it seems in many other respects probable. But there are two difficulties. The one is that we do not see why a rubber once crystallised by stretching should become amorphous again on relaxation at a temperature far below the melting-point of spontaneously frozen rubber. Secondly, we do not see what force is strong enough to retract the rubber, no matter how carefully we observe. E. Mack has tried to explain it by the attraction of hydrogen atom to hydrogen atom; others by appealing to the Brownian movement of the chain (Kurt H. Meyer and others). Both conceptions seem possible, but no really convincing argument, I think, has as yet been given. So we cannot yet offer a really good explanation of the rubber-like elasticity and of the X-ray spectrographical facts so closely connected with it.

The same difficulties in the explanation of the X-ray phenomena and the elasticity are met in synthetic substances with a rubber-like extensibility.

GENERAL DISCUSSION

Professor K. H. Meyer (*Geneva*) said: "Speaking of 'probability' and 'certainty' in the determination of elementary cells and spacial models, let me emphasise, that the cell dimensions of cellulose," rubber," and silk fibron⁴⁰ have been based on diagrams with subjects of a higher order of orientation. Such subjects, generally thin films, show an orientation not only parallel to the fibre axis, but also in the plane perpendicular to this axis. One can therefore calculate with full *certainty* the three density periods and the elementary cell.

As to the abnormal specific weight, which follows from the dimensions of the rubber cell of Mark and Susich, recent experiments in Geneva showed, that this discrepancy is due to a simple experimental error.

From a general point of view, I desire to observe in regard to the "probability" or "certainty" of our spacial models, that Katz only takes into account the Roentgenographical arguments and we quite agree, that with these data alone one cannot attain practical certainty in such complicated molecules. But if one takes into account the chemical evidence, for instance the cellulose and cellulose formula of Haworth and the rubber formula of C. O. Weber in connection with other physical properties (*e.g.*, tenacity, double-refraction, etc.) one arrives at only one possible, and therefore final solution, in which only slight variations of the atomic parameters can be allowed.

Professor H. Mark (*Wien*) said: Dr. Katz's contribution gives the impression that the ideas on the structure of such highly polymerised substances as cellulose, rubber, keratin, etc., are as yet not at all well

³⁹ Mark and Susich, *Z. physik. Chem.*, 1929, **4B**, 431.

⁴⁰ Mark and Susich, *Koll. Z.*, 1928, **46**, 11.

⁴¹ Kratky, *Z. physik. Chem.*, 1929, **5B**, 297.

founded on actual experiment. He therefore speaks of the "hypothesis" of the long chain model and points out, that it is mainly of importance for teaching, and not so much for research.

I think we may justifiably attribute to these models (which have been worked out during recent years with increasing accuracy by a large number of authors), a somewhat high degree of truth. I quite agree with Dr. Katz that we must needs improve our ideas here and there, work out the exact positions of the different atoms in the lattice, and explore the accurate dimensions and shape of the molecules in solution, but I am quite convinced that the present point of view will not be totally changed, so that we shall have to start to work in quite another direction. The increasing confidence given to our present models of long-chain molecules is based, not so much solely on the work on highly polymerised substances, as on the facts that, during recent years, we have learned a great deal about the solid state, and that our general knowledge of the structure of organic crystals has considerably increased. This very important development is, in the first place, due to the systematic work of Sir W. H. Bragg and Professor W. L. Bragg and their collaborators, and was carried out mostly in the Royal Institution in London, in the Physical Laboratory in Manchester, and in the Mineralogical Institute in Cambridge. It is well known that, by considerably improving experimental methods, and working out quite new means of evaluating the relative and absolute intensity measurements, one is now able to fix the atomic positions, even in very complicated lattices, such as, e.g., hydroquinone, dinitrobenzene, chrysene, etc. In the case of the cellulose, Andress and von Susich have carefully measured the relative intensity of all interference spots, and Hengstenberg has strengthened their calculations by the measurement of the more important absolute intensity values. These figures were evaluated by the normal method of structure factor, and led to the present conception as to the positions of the different atoms in the unit cell. To bring the situation up to date, it would be necessary to apply the Fourier's analysis method to these experimental data, which would of course be a very important task. It is quite probable that such a calculation would change the position of different atoms in the lattice, and bring about a closer agreement with the experimental facts, but I do not think that a fundamentally different structure would be derived.

At this stage it is important to point out, that it is not by any means the X-ray evidence alone which leads to our present conception of the structure of high polymeric substances. A large number of independent arguments come from investigations in organic chemistry and physical chemistry, which lead to exactly the same result. I mention the synthesis of main valence chains by Staudinger and his co-workers, the degradation of cellulose by Freudenberg, Haworth and their collaborators, the preparation of several new addition compounds by Hess and Tregus, and the investigation of different physico-chemical properties by Berl, Herzog, Katz, Kraemer, Mark, Meyer, Ostwald, Signer, Svedberg and a number of other authors. All these studies, starting from quite different directions, converge in their results upon a model which can surely be called a very good approximation to the truth, and can be regarded as a trustful basis for future work.

I would like to recall that the diffraction of electrons on high polymeric substances, which has been investigated by Dauvillier, Kirchner, Mark, Motz, Taylor-Jones and Trillat offered at first very serious difficulties to the long chain model of cellulose. In the end Mark and Trillat and at the same time Hengstenberg and Wolt gave vent to the suspicion, that the very sharp interference spots obtained with these substances are not due to cellulose, but may be caused by an impurity. Accurate measurements of Mark, Motz, Natta and Trillat showed later that, in fact, these patterns are produced by grease-like substances, which are extended on the surface of the films in very thin layers. If one removes these films, the diagram

vanishes, if one produces them the diagram appears. The same has been found on metallic films, and may serve to explain several features, which are not yet quite clear.

On the other hand, I quite agree with Dr. Katz, that one must be very careful, in drawing conclusions from fibre diagrams and, to a still higher degree, from ring diagrams. Everybody who uses the X-ray method in the field of high polymeric substances (and is therefore forced to interpret interference patterns of diagrams which often show only a few points or rings) should work out at least one structure in the field of normal organic lattices, because only in doing this can he get the experience, which seems to be indispensable if one wants to evaluate diagrams of high polymeric specimens. I agree also with Dr. Katz, that one should, with great caution, apply results derived from diagrams with few spots or rings, and I do not think that it is possible to clear up the exact shape of molecules in a liquid by measuring the diameter of only two diffuse rings.

Dr. R. Houwink (*Eindhoven*) said: May I point out, in variance with Dr. Katz' opinion, that not all organic substances which show rubber-like extensibility seem to have a long-chain molecule. In this connection I refer to my paper,⁴² on the high-elasticity of three-dimensionally polymerised materials.

Dr. W. H. Carothers (*Wilmington*) said: Linear condensation polymers of simple unsubstituted types are almost invariably sufficiently crystalline to furnish well-defined powder diffraction patterns, and they can also usually be got in a form suitable to yield fibre patterns as well. Since with relatively few starting materials the length of the unit A-B in the chain A-B-A-B-A-B, etc., can be varied at will over a very wide range, such polymers furnish a vast family of excellent models for the study of X-ray behaviour. As yet they have received relatively little attention. It is a curious fact also that in some cases sharp patterns can be obtained from a mixture of reactants A, B, A', B'. This leads to four structural units A-B, A'-B', A-B', and A'-B, all of different lengths, and since they must be arranged at random in the polymer chains, the probability of finding two identical molecules of say 50 units in a sample of moderate size is very small. The co-existence of crystallinity with such a degree and type of heterogeneity seems difficult to reconcile with the conventional ideas of crystallinity.

⁴² This vol., p. 131.

* Professor Katz' reply, which was received after going to press, will be found at the end of the Report.

THE FORMATION OF HIGH POLYMERS OF UNSATURATED SUBSTANCES.¹

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I. Influence of the Substituents upon the Polymerisation-Capacity of Unsaturated Compounds.

A great number of unsaturated compounds, containing a C=C double bond or a carbonyl-group² have the tendency to polymerise—i.e., to transform themselves into substances of unchanged composition but with a much higher molecular weight. The strength of this tendency is very different with different compounds and depends essentially on the nature of the substituents adjacent to the double bond. Ethylene, for instance, is a stable compound, whereas its derivatives containing "negative" substituents are unstable and easily polymerised, e.g. styrene, vinyl chloride, vinyl acetate and acrylic ester. The influence of the same substituents is different in the case of the C=C double bond and in that of the carbonyl-group. In the latter case, the simplest compound, formaldehyde, is the least stable of all. The introduction of phenyl and especially of chlorine into the molecule of formaldehyde cause the tendency to polymerisation to disappear. (Benzaldehyde and phosgene for instance are stable compounds.) The substitution of

TABLE I.—POLYMERISATION TENDENCY OF ETHYLENE DERIVATIVES AND OF CARBONYL COMPOUNDS.

C = C Compounds	Polymerises.	C = O Compounds.	Polymerises.
1. $\text{CH}_2 = \text{CH}_2$	With some difficulty.	1. $\text{CH}_2 = \text{O}$	Very easily.
2. $\text{CH}_3 \cdot \text{CH} = \text{CH}_2$	With difficulty.	2. $\text{CH}_3 \cdot \text{CH} = \text{O}$	Easily.
3. $(\text{CH}_3)_2 \cdot \text{C} = \text{CH}_2$	Easily.	3. $(\text{CH}_3)_2 \text{C} = \text{O}$	Not: condensation only.
4. $\text{CH}_2 = \text{CH} \cdot \text{CH} = \text{CH}_2$	Very easily.	4. $\text{CH}_2 = \text{CH} \cdot \text{CH} = \text{O}$	Very easily.
5. $\text{C}_6\text{H}_5 \cdot \text{CH} = \text{CH}_2$	Very easily.	5. $\text{C}_6\text{H}_5 \cdot \text{CH} = \text{O}$	Not: condensation only.
6. $\text{CH}_3\text{O} \cdot \text{CO} \cdot \text{CH} = \text{CH}_2$	Very easily.	6. $\text{CH}_3\text{O} \cdot \text{CO} \cdot \text{CH} = \text{O}$	Very easily.
7. $\text{CH}_3 \cdot \text{CO} \cdot \text{CH} = \text{CH}_2$	Very easily.	7. $\text{CH}_3 \cdot \text{CO} \cdot \text{CH} = \text{O}$	Easily.
8. $\text{CH}_3 \cdot \text{CO} \cdot \text{OCH} = \text{CH}_2$	Easily.	8. $\text{CH}_3\text{OCH} = \text{O}$	Not.
9. $\text{Cl}_2 \cdot \text{C} = \text{CH}_2$	Easily.	9. $\text{Cl}_2 \cdot \text{C} = \text{O}$	Not.
10. $\text{O} = \text{C} \cdot \text{CH}_2$	Easily.	10. $\text{O} = \text{C} = \text{O}$	Not.

¹ Compare the author's monograph *Die hochmolekularen organischen Verbindungen-Kautschuk und Cellulose*, Springer, Berlin, 1932. Quotations "Book, at p. " below refer to this monograph.

² We do not discuss in this paper the polymerisation of substances whose unsaturated groups are other than C=C, e.g. such as C=N or C=S.

a carbonyl or a carboxyl group makes the molecule unstable again—as shown, *e.g.* by glyoxylic acid, glyoxal and methyl glyoxal. Table I. summarises the results.

When more than one substituent is present in an ethylene derivative, one usually finds that the symmetrical compounds are more stable than the asymmetric ones. The asymmetric ethylene dichloride polymerises for example much more readily than the corresponding symmetric compound: for instance crotonic ester is stable, the methacrylic ester is not.³

Unsaturated compounds with conjugated double bonds are generally more reactive than those with isolated double bonds. Butadiene, for instance, polymerises much more easily than ethylene or ethyl-ethylene, acrolein much more readily than propionic-aldehyde. If a methyl group is introduced into a molecule with conjugated double-bonds with α -position, the polymerisation-tendency becomes weaker; it is raised, however, by the same substituent in a β -position.

TABLE II.—POLYMERISATION TENDENCY OF DIFFERENT DERIVATIVES OF ETHYLENE.

Initial Substance, easily Polymerised.	Methyl-group in α -position Polymerising hardly or not at all.	Methyl-group in β -position Polymerising easily.
$\text{CH}_2=\text{CH} \cdot \text{CH}=\text{CH}_2$	$\text{CH}=\text{CH} \cdot \text{CH}=\text{CH}_2$ CH_3	$\text{CH}_2=\text{C} \cdot \text{CH}=\text{CH}_2$ CH_3
$\text{CH}_2=\text{CH} \cdot \text{CH}=\text{O}$	$\text{CH}=\text{CH} \cdot \text{CH}=\text{O}$ CH_3	$\text{CH}_2=\text{C} \cdot \text{CH}=\text{O}$ CH_3
$\text{CH}_3 \cdot \text{CH} \cdot \text{C}=\text{O}$ OH	$\text{CH}=\text{CH} \cdot \text{C}=\text{O}$ CH_3 OH	$\text{CH}_2=\text{C} \cdot \text{C}=\text{O}$ CH_3 OH
$\text{CH}_3=\text{CH} \cdot \text{C}=\text{O}$ CH_3	$\text{CH}=\text{CH} \cdot \text{C}=\text{O}$ CH_3 CH_3	$\text{CH}_2=\text{C} \cdot \text{C}=\text{O}$ CH_3 CH_3

The polymerisation of some unsaturated compounds occurs spontaneously even at or slightly above room temperature. Formaldehyde, styrene, and acrylic ester provide examples of this behaviour. Polymerisation is often favoured by light, as in the cases of vinylacetate and particularly of vinyl chloride and vinyl bromide. Many unsaturated compounds polymerise only with catalysts. An appropriate catalyst is Florida-earth; halogenides of metals or non-metals possessing a tendency to form complexes are also good catalysts, *e.g.*, boron fluoride, tin tetrachloride and aluminium chloride. Silicon tetrachloride and phosphorus oxychloride, although belonging to the same class of acid chlorides, have no tendency to form complexes and therefore do not strongly catalyse polymerisation-reactions.⁴ Among the unsaturated compounds which polymerise only with catalysts are *iso*-butylene, anethole and indene.

Some polymerising unsaturated substances form dimeric, trimeric, sometimes tetrameric products—examples are diphenyl-ethylene, diphenyl-ketene, phenyl-*iso*-cyanate; others give high polymers, *e.g.*,

³ A. Michael, *J. prakt. Chemie*, 1899, **60**, 382.

⁴ Cf. H. Staudinger and H. A. Bruson, *Annalen*, 1926, **447**, 110.

vinyl chloride, vinyl ester, vinyl acetate. A certain number of unsaturated compounds yield low or high polymers according to the polymerisation conditions—it is for instance possible to convert styrene into distyrene by certain catalysts,⁶ whereas the spontaneous polymerisation of styrene—or polymerisation catalysed by other substances—yields highly polymerised “poly-styrenes.” Dimethyl ketene and cyclopentadiene give dimolecular products by spontaneous polymerisation; by addition of catalysts it is possible to obtain high polymers of these substances too.⁶

II. The Importance of Synthetic High-Polymers.

In the following, polymers of the ethylene derivatives and of carbonyl-compounds alone will be considered. Among all the synthetic high polymers they offer remarkable scientific and technical interest.

Many of them have been investigated from the *scientific* point of view because of the analogies they offer to many natural high-molecular products and their derivatives. They dissolve with strong swelling and form colloidal solutions; they belong thus to the class of lyophilic colloids. It was found of great advantage to use synthetic products of this kind, because of their relatively simple structure and their greater stability, for studying the colloidal properties in general. By investigating the chemical constitution of synthetic high-molecular substances it was found that their colloidal properties—such as swelling capacity and viscosity of their solutions—depend only upon the size and shape of their macro-molecules. These experiments led to valuable conclusions as to the structure of natural high-molecular products, for instance of caoutchouc⁷ and cellulose,⁸ which are built-up in the same manner as the synthetic high polymers. The colloidal properties of these natural products are also functions of the size and form of their macro-molecules.

The synthetic high polymers, which are obtained by polymerisation of unsaturated compounds, offer great interest also from the technical point of view. Since many of their properties are similar to those of the high-molecular natural products, they can be used as more or less complete substitutes for them. It is not improbable, that sooner or later a way will be discovered to prepare artificial fibres from synthetic high-molecular products, because the strength and elasticity of natural fibres depend exclusively on their macro-molecular structure—i.e., on their long thread-shaped molecules. Industry is therefore keenly interested in the investigation of the constitution of high-molecular products and of the nature of the polymerisation process.

III. Homœopolar and Heteropolar Molecular Colloids.

The aim of the following investigations was to elucidate the constitution of highly polymerised substances and to explain their specific properties. Therefore, the very simple high-polymeric substances have been used, which offered the greatest chance of finding out the apparently so complicated relations between structure and colloidal properties.

⁶ Stobbe and Posnjak, *Annalen*, 1910, 311, 292.

⁷ As to poly-cyclopentadiene see H. Staudinger and H. A. Bruson, *Annalen*, 1926, 447, 110; as to poly-dimethyl ketene, H. Staudinger, *Helv. chim. acta*, 1925, 8, 306.

⁸ See H. Staudinger, *J. R. J. Transactions*, 1935, 10, No. 3.

⁹ H. Staudinger, *Trans. Faraday Soc.*, 1933, 29, 18; *Naturw.*, 1934, p. 797.

Furthermore, we selected such synthetic polymers whose colloidal properties were closely related to those of high-molecular natural products. We have therefore especially investigated the polystyrenes,⁹ in which the swelling resembles that of rubber and which give also highly viscous solutions. Polystyrenes are saturated hydrocarbons and on account of their greater stability can therefore be more favourably examined than the unsaturated caoutchouc. By polymerising vinyl acetate we obtained high-polymeric esters of which the colloidal properties were very near to those of the cellulose acetates.

One of our principal interests was to learn how the properties of the different monomeric substances are reflected in the properties of organic types of high polymers. We know, for instance, that in the low-molecular state there is a substantial difference between the properties of the homœopolar compounds—for instance hydrocarbons, ethers and esters—and those of the heteropolar substances, such as the salts of organic acids and bases. Furthermore the chemical and physical properties of homœopolar compounds are characteristically changed by certain substituents—the introduction of a hydroxyl group for instance renders insoluble volatile compounds water-soluble and non-volatile.

For this purpose we investigated in addition to homœopolar high-molecular substances (hydrocarbons, ethers, esters), which are soluble in organic solvents, also heteropolar high molecular polymers. Readily prepared representatives of this class are the polymers of the acrylic acid. The heteropolar molecular colloids, such as sodium-polyacrylate are soluble in water and have colloidal properties essentially different from those of the homœopolar polymers—for instance polystyrene or polyvinyl-acetate. Their investigation has revealed much which proved to be important for the understanding of the colloidal properties of solutions of cellulose xanthogenate, of cellulose in Schweizers solution and also of proteins—which are all heteropolar molecular colloids too.

Synthetic high polymers with hydroxyl groups are represented by the polyvinyl-alcohols, obtained by saponification of polyvinyl-esters. These products can be considered as prototypes of starch.

TABLE III.—TYPES OF SYNTHETIC HIGH POLYMERS.

Basic Molecule.	Polymeric Compound.	Belonging to the Polymer-Homologous Series of:	Colloidal Character.	Model of
CH_2O	$\dots -\text{CH}_2-\text{O}-(\text{H}_2-\text{O})_x-\text{CH}_2-\text{O}-\dots$	Poly-oxy-methylenes.	High-molecular unsoluble substances.	Cellulose.
C_6H_5 $\text{CH}=\text{CH}_2$	$\text{C}_6\text{H}_5 \quad \text{C}_6\text{H}_5 \quad \text{C}_6\text{H}_5$ $\dots -\text{CH}-\text{CH}_2-(\text{CH}-(\text{H}_2))_x-(\text{H}-\text{CH}_2-\dots$	Polystyrenes.	Homœopolar molecular colloids. Organosols.	Caoutchouc.
OH $\text{CH}=\text{CH}_2$	$\text{OH} \quad \text{OH} \quad \text{OH}$ $\dots -\text{CH}-\text{CH}_2-(\text{CH}-\text{CH}_2)_x-\text{CH}-\text{CH}_2-\dots$	Polyvinyl alcohols.	Molecular colloids with coordinative covalencies; Hydrosols.	Starch.
COO^-Na^+ $\text{CH}=\text{CH}_2$	$\text{COO}^-\text{Na}^+ \quad \text{COO}^-\text{Na}^+ \quad \text{COO}^-\text{Na}^+$ $\dots -\text{CH}-\text{CH}_2-(\text{CH}-\text{CH}_2)_x-\text{CH}-\text{CH}_2-\dots$	Polyacrylic sodium.	Heteropolar molecular colloids. Hydrosols.	Cellulose xanthogenates and protein solutions.

⁹ See H. Staudinger and others, *Ber.*, 1929, **62**, 241; H. Staudinger and W. Heuer, *Book*, p. 157.

IV. Hemicolloids, Mesocolloids, Eu colloids.

The polymerisation of these simple unsaturated compounds to high-polymers is based on the chemical combination of a great number of unsaturated basic molecules (in German: "Grundmoleküle") to a long thread-shaped "macro-molecule." The number of basic molecules or repeating units contained in a single thread depends on the nature of the substance and the conditions of polymerisation. A polymeric molecule can be formed out of 2, or 100, or 1000 basic molecules. The highest known synthetic polymers are built up from 5 to 10,000 molecules.

One and the same initial substance, for instance styrene, vinyl acetate or acrylic ester—can be induced by variation of conditions, *e.g.*, temperature or nature of catalyst, to form polymers with different chain-lengths, although constructed according to the same principle. We call these products of identical structure, differing only in the length of the chain-molecules, a "polymeric-homologous series."¹⁰ Since the physical properties of high polymers change with the length of the macro-molecules, it is possible to prepare, from one and the same initial substance, by changing the conditions of polymerisation, high polymers with very different physical properties. This fact is of great technical importance. One can discriminate between three main groups of molecular colloids, corresponding to different lengths of the fibre-molecules.¹¹

1. Hemicolloids.—We give this name to polymers with a molecular weight up to 10,000, corresponding to an order of polymerisation, equal to 20 to 100. Their chain-molecules have a length from 50 up to about 250 Å. With such relatively short molecular threads the colloidal properties are not yet very pronounced. The hemicolloids dissolve without swelling, their solutions have a low viscosity, and obey the Hagen-Poiseuille law. The solids are powdery or gluey masses; filaments or films prepared from them have little tensile strength and are easily broken.

2. Mesocolloids.—The order of polymerisation of these fibre-molecules ranges from 100 up to about 1000, their molecules having a length from 250 up to about 2500 Å. Their properties are intermediate between those of the hemicolloids and of the eu colloids.

3. Eu colloids.—These substances have macro-molecules with a polymerisation order over 1000, the length of the molecules being over 2500 Å. The longest thread-molecules, which so far have been prepared synthetically, are about 1μ long. The eu colloids have the characteristic properties of lyophilic colloids. Their dissolution is accompanied by an intense swelling, and their solutions are highly viscous, even at low concentrations; they do not obey Einstein's law, and their flow-phenomena are not those of a normal liquid. The solid eu colloidal substances are very tough and hard. The technically most important polymers belong to this group. They show a high capacity for film-formation, and are often highly elastic.

If eu colloids are subjected to an appropriate treatment—for instance a thermal cracking-process or a decomposition by oxidation—products

¹⁰ H. Staudinger, *Angewandte Chem.*, 1929, **42**, 69.

¹¹ The classification of colloids was discussed in my lecture before the International Congress of Chemistry, in Madrid, 1934. See further, *Ber.*, 1926, **59**, 3019; 1929, **62**, 2893; and a forthcoming communication (No. 117) in the same periodical (*Ber.*, 1935, **68**, 1582).

with shorter molecules can be obtained, having mesocolloidal or hemicolloidal properties. The synthetic hemicolloids—for instance hemicolloidal polystyrenes or polyvinyl acetates—are thus obtainable either by direct polymerisation of the monomeric substances under suitable conditions, or by partial decomposition of the eu colloids. On the other hand natural hemicolloids and mesocolloids can only be obtained by partial decomposition of the natural eu colloids—cellulose or its derivatives. This time no alternative way of getting the same products by synthesis is available.

Whereas some unsaturated compounds—styrene, acrylic ester, vinylacetate—can give hemi-, meso- or eu colloidal products, according to the special conditions of polymerisation, some other compounds have so far yielded hemicolloidal products only. Indene, cumarone, anethole are substances of this kind, giving polymers with relatively short chain-molecules only.

The exact knowledge of the polymerisation process, and especially of the polymerisation order, is very important from the technical point

TABLE IV.

Basic Molecule.	Conditions of Polymerisation.	Solubility of the Polymer.	Kind of the Polymeric Products.	Order of Polymerisation.	Reference.
$\text{CH}_2=\text{C}(\text{CH}_3)_2$	Catalytic.	Eas. soluble in C_6H_6 , CCl_4 etc.; insoluble in acetone.	From hemicoll. to eu coll.	10-1000	<i>Helv. chim. acta</i> , 1930, 13 , 1373.
$\text{CH}_2=\text{CH} \cdot \text{C}_6\text{H}_5$	Spontaneous and catalytic.	Eas. soluble in C_6H_6 , CCl_4 , etc.; insoluble in acetone.	Eucoll. to hemicoll.	10-5000	<i>Ber.</i> , 1929, 62 , 241; 2012, 2921; <i>Book</i> , p. 157.
$\text{CH}_2=\text{CH} \cdot \text{CH}=\text{CH}_2$	Thermal and catalytic.	Eas. soluble in C_6H_6 , CCl_4 .	From hemicoll. to eu coll.	10-1000	<i>Ber.</i> , 1934, 67 , 1171.
$\text{CH}_3\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}=\text{CH} \cdot \text{CH}_3$	Catalytic.	Sol. in C_6H_6 , CCl_4 .	Hemicoll.	10-200	<i>Helv. chim. acta</i> , 1929, 12 , 972; <i>Annal.</i> , 1934, 517 , 73.
$\text{C}_6\text{H}_5 \begin{array}{c} \diagup \text{CH} \\ \diagdown \text{CH} \end{array} \text{CH}$	Catalytic	Sol. in C_6H_6 , CCl_4 .	Hemicoll.	10-100	<i>Helv. Chim. acta</i> 1929, 12 , 934.
$\begin{array}{c} \text{CH}=\text{CH} \\ \quad \quad \\ \text{CH}=\text{CH} \quad \text{CH}_2 \end{array}$	Spontaneous and catalytic.	Sol. in organic solvents	Dimolecular hemicoll.	2 to ca. 100	<i>Annal.</i> , 1926, 447 , 97, 110.
$\text{CH}_2=\text{CH} \cdot \text{Br}$	Photochemical and catalytic.	Hardly soluble.	Hemicoll.	50-200	<i>Helv. chim. acta</i> , 1930, 13 , 803, 832.
$\text{CH}_2=\text{C} \begin{array}{c} \diagup \text{COCH}_3 \\ \diagdown \text{CH}_3 \end{array}$	Spontaneous and catalytic.	Eas. soluble in C_6H_6 , CCl_4 .	Eucoll. and mesocoll.	500-1500	<i>Ber.</i> , 1934, 67 , 1773.
$\text{CH}_2=\text{CHO} \cdot \text{CO} \cdot \text{CH}_3$	Catalytic (espec. peroxides)	Eas. soluble in C_6H_6 and acetone; insoluble in CCl_4 .	Hemicoll. and eu coll.	50-1000	<i>Ber.</i> , 1927, 60 , 1782; <i>Annal.</i> , 1931, 488 , 8.
$\text{CH}_2=\text{CH} \cdot \text{COOCH}_3$	Spontaneous and catalytic (peroxides).	Soluble in C_6H_6 and acetone; insoluble in ether.	From eu coll. to hemicoll.	50-1000	<i>Helv. chim. acta</i> , 1929, 12 , 1107.
$\text{CH}_2=\text{CH} \cdot \text{COOH}$	Spontaneous; thermal.	Sol. in H_2O .	From hemicoll. to eu coll.	100-1000	<i>Ber.</i> , 1931, 64 , 2091; <i>Book</i> , p. 333; <i>Annal.</i> , 1933, 502 , 201.
$(\text{CH}_3)_2\text{C}=\text{C}=\text{O}$	Spontaneous and catalytic.	Eas. soluble in organic solvents.	Dimolecular hemicoll.		<i>Helv. chim. acta</i> 1923, 6 , 306.
$\text{CH}_2=\text{O}$	Spontaneous; catalytic.	Insoluble; hardly soluble.	Eucoll. and hemicoll.	20-100	<i>Helv. Chim. acta</i> , 1925, 8 , 41; <i>Annal.</i> , 1929, 474 , 145; <i>Book</i> , p. 224.

* Often only limited swelling polymers are formed; vide H. Staudinger and W. Heuer, *Ber.*, 1934, **67**, 1171.

of view: the hemicolloids and the euolloids having different physical properties, their technical uses are quite different too. For preparing varnishes, for instance, chiefly hemicolloids are used, because the high viscosity of euolloidal solutions is undesirable for this purpose. For artificial resins, from which great tensile strength is highly desirable euolloids are the most suitable materials.

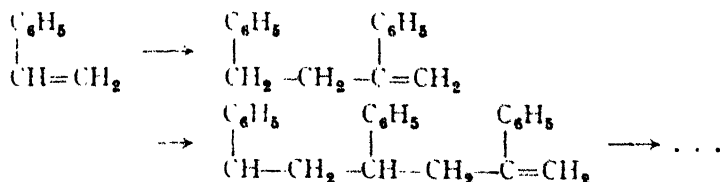
Table IV. gives a list of the simple synthetic high polymers which have so far been investigated in our laboratories in Freiburg, together with their most important physical properties.

We see from Table IV. that high polymers with most different colloidal properties can be obtained synthetically. The number of synthetic substances of this kind has been further increased in recent years, since it was found possible to obtain "mixed" polymers by polymerising mixtures of different unsaturated substances. It is interesting that unsaturated compounds, such as maleic anhydride, which do not polymerise by themselves, form high-polymeric products, when mixed with polymerisable substances, for instance with styrene.¹² These mixed products are of great technical interest; but we do not intend to discuss them further here, because their complicated structure makes them less suitable for the investigation of the relations between colloidal phenomena and molecular structure.

V. The Process of Polymerisation.

The transformation of unsaturated monomeric substances into polymers can take place in different ways. One is characterised by the conservation of the atomic arrangement of the monomeric substance—as, for instance, in the cases of formaldehyde transformed into trioxymethylene, tetraoxymethylene, or the polyoxymethylenes. Another way is the linking together of two molecules after the shifting of a hydrogen atom, *e.g.*, the transformation of acetaldehyde into aldol, of formaldehyde into sugar or of styrene into distyrene. We call the first reactions *true polymerisations*, these of the second kind *condensation-polymerisations*.¹³

The question: how do the high-polymeric products arise has been answered differently. Some investigators¹⁴ conceived that an unsaturated molecule can form a link with another molecule when a hydrogen atom shifts along the chain. The same process is repeated many times, until the high-polymeric chain is formed. The formation of polystyrenes, according to this theory, occurs in the following way:



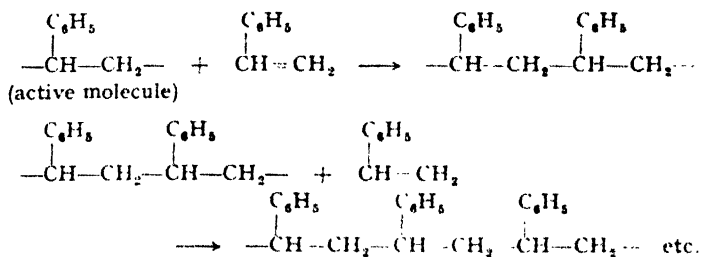
¹² Wagner-Jauregg, *Ber.*, 1930, **62**, 3213; Mixed polymers became recently an object of manifold technical interest; the latest patents are reviewed by E. Sauter, *Kolloid Z.*, 1935, **71**, 357. Mixed polymers formed by SO_2 with unsaturated compounds are described by H. Staudinger and B. Ritzenthaler, *Ber.*, 1935, **68**, 455; Peroxides as mixed polymers, *see* H. Staudinger, *Ber.*, 1925, **58**, 1075.

¹³ H. Staudinger, *Ber.*, 1920, **53**, 1081.

¹⁴ G. S. Whitby and J. R. Katz, *J. Amer. Chem. Soc.*, 1928, **50**, 1160; *see also* W. Gallay, *Kolloid Z.*, 1931, **57**, 2.

This theory implies that the formation of the high-polymeric products occurs in steps, each corresponding to a specific compound capable of isolation, as such. In fact, processes of this kind occur, but they lead to relatively low-molecular products and never to high polymers.¹⁵

The formation of real high polymers must be explained in another way; a molecule of the monomeric substance becomes activated—by heat, light or by a catalyst—and can therefore react with a second molecule. The newly-formed molecule has an "active point" on each its ends, and the polymerisation process can thus proceed further, until an unknown side-reaction makes the active centres disappear. The following scheme describes this process:



The intermediate stages of the polymerisation are in this scheme unsaturated radicals, highly reactive, and therefore incapable of isolation. The reaction has thus the features of a *chain reaction*,¹⁶ comparable with the well-known chain-reactions of low-molecular substances. Only by such a mechanism can extremely high-molecular products of a eucolloid nature be formed synthetically; it could not be done by a process of the kind described by the first scheme.

The assumption that the polymerisation is a chain-reaction is confirmed by the following facts: From the very beginning of the polymerisation-process high-molecular products are already present in the reacting system; the intermediary products which one would expect to occur according to the first scheme, have not been isolated. One can easily prove these statements, *e.g.*, in the case of polyacrylic acid, which is insoluble in the monomeric acid. If we analyse the first small amounts of the polymeric product which are precipitated from the polymerising liquid, we find them to be already very high-molecular. The liquid still consists of pure monomeric acid, without any traces of an intermediate product.¹⁷

When styrene is polymerised, it changes slowly, first into a highly viscous solution, later into a solid gel. Finally, solid glassy polystyrene is formed from the gel. No stable intermediate products with shorter chains are formed in the course of the polymerisation: the chain-reaction from the very beginning yields high-molecular polymers with a chain-length equal to that of the final product. W. Frost¹⁸ demonstrated this some time ago. He separated from time to time polymerised

¹⁵ H. Staudinger and A. Steinhöfer, *Annalen*, 1935, **517**, 41, showed that distyrene and tristyrene cannot add further molecules of styrene to form polystyrenes.

¹⁶ H. Staudinger and H. W. Kohlschütter, *Ber.*, 1931, **64**, 2093; also *Book*, pp. 149, 223, 255, 289.

¹⁷ H. Staudinger and H. W. Kohlschütter, *Ber.*, 1931, **64**, 2093.

¹⁸ These experiments were made by W. Frost in Freiburg in 1929; they have now been published (*Ber.*, 1935, **68**, 2351).

styrene from the reacting mass, by addition of alcohol, and determined the amount and the order of polymerisation of the product. Table V. shows that the viscosity of a 1 per cent. solution of the polymerised styrene remains nearly the same from the beginning to the end of the polymerisation process, a proof that completely polymerised products are formed already in the first stages of the process.

TABLE V.—COURSE OF POLYMERISATION OF STYRENE.

(Reaction-products determined gravimetrically.)

Time of Heating.	Per Cent. of Polystyrene.	Relative Viscosity of a 1 Per Cent. Solution in Benzene at 20° C.
At 100° C.		
12 hours.	19.4	3.82
25 "	40.6	3.91
240 "	96.0	4.22
At 60° C.		
6 days.	10.7	7.78
20.5 "	41.2	7.61
35 "	74.3	7.85
175 "	92.1	8.14

The polymerisation of styrene differs from that of acrylic acid only because the polymer is soluble in the monomeric substance, whereas the polymeric acrylic acid at once precipitates from the monomeric acid.¹⁹ This is why the polymerisation of styrene at first gives a highly viscous liquid. In this intermediate stage of the polymerisation, the macro-molecules of the polystyrene are dissolved in the monomeric styrene. The properties of such a "gel"-solution are identical with those of the solution of polystyrenes in other organic solvents, *e.g.*, in benzene. The polymeric molecules, which are contained in liquid styrene, have the same length as those contained in the final product of the polymerisation, the solid polystyrene-glass.

High-molecular polymers can be obtained also in other ways. Carothers²⁰ showed, for instance, that they are obtainable by "polycondensation" of poly-basic acids with glycols. Polycondensations do not yield, however, eucolloidal products, like the chain-polymerisations of unsaturated compounds, because with growing length of the macro-molecule the chances for a further condensation-reaction become smaller and smaller. That is why so far only products with a molecular weight up to 20,000-30,000 have been prepared by polycondensation, whereas by chain-reactions, as mentioned above, products with a molecular weight up to 500,000 and more may be obtained.

VI. Constitution of the Synthetic High Molecular Products.

When high-polymeric substances were first investigated there was much discussion as to whether these substances are built up from *macromolecules*,²¹ or from *micelles*.²² Without referring much to this discussion, we may mention that the macromolecular structure of high-

¹⁹ Kronstein (*Ber.*, 1902, **35**, 4150) thought that observations of this kind must lead to a distinction between two types of polymerisation; compare in this connection, H. Staudinger, *Ber.*, 1920, **53**, 1081.

²⁰ W. N. Carothers, *J. Amer. Chem. Soc.*, 1929, **51**, 2548 and later.

²¹ H. Staudinger and J. Fritsch, *Helv. Chim. Acta*, 1922, **5**, 785; *Ber.*, 1926, **59**, 3019; *Z. angewandte Chemie*, 1929, **42**, 37, 67.

²² P. Karrer, *Polymere Kohlenhydrate*, Leipzig, 1925; M. Bergmann, *Ber.*, 1926, **59**, 2973; K. H. Meyer, *Z. angew. Chemie*, 1928, **41**, 935.

molecular substances was first definitely proved by the experiments on poly-oxymethylenes.²³

The principal question to be answered in the case of a high-polymer giving a colloidal solution is: are the dissolved particles micelles, as first supposed, or are they identical with the macro-molecules of the polymer? The essential property by which a macro-molecule differs from a micelle is that, in a macro-molecule, all the atoms are linked together by normal co-valent links, as in ordinary organic molecules. The only difference between macro-molecular and low-molecular substances is that, whereas the latter consist of absolutely identical molecules, the former are built up of a mixture of polymeric homologous molecules. Because of the resemblance between the physical properties of all these molecules, it appears impossible to separate the polymerised substance into its single chemically pure components.²⁴ A *micelle*, on the other hand, is a particle built up from small single molecules held together by van der Waals' attraction forces.²⁵

It was thus necessary to investigate the source of the colloidal properties of the solutions of high-molecular substances, e.g., their high viscosity and their swelling capacity. Are these properties due to a micellar structure, or are they to be explained by the great size of the molecules? It is a very important question, because the colloidal properties of many solutions of macro-molecular substances (e.g., of rubber, in benzene, or of sodium acrylate in water), are similar to those of some undoubtedly micellar solutions, e.g., of soaps. Both kinds of solution are highly-viscous, and do not obey the law of Hagen and Poiseuille. The dissolution of both is accompanied by a strong swelling. Important differences exist, however, for instance, in the hardness and tensile strength of the solid substances and in the stability of the solutions.

The resemblance in the colloidal properties of the different kinds of solutions must be ascribed to the fact that all contain dissolved particles in the shape of long threads. The differences are explained by the assumption, that these particles are *thread-micelles* in the case of soaps, but *thread-molecules* in the case of rubber, and polyvalent *thread-ions* in the case of sodium polyacrylate. An understanding of the whole of the properties of these colloids can be obtained only by elucidation of the constitution of their colloid particles.

The macro-molecular structure of the colloid particles of high-molecular substances has been proved in the same way as that by which the structure of ordinary low-molecular organic substances is usually investigated. By changing the conditions of polymerisation it was possible to obtain, from one and the same initial unsaturated monomeric substance, a whole *polymeric series* of different polymerisation-products. In studying a series of this sort, one finds that the physical properties (of the solid products as well as of their solutions) change gradually with growing length of the molecule. The relations between physical properties and chain-length are

²³ H. Staudinger and U. Fütty, *Helv. Chim. Acta*, 1925, 8, 41; also H. Staudinger and R. Signer and others, *Annalen*, 1929, 474, 145.

²⁴ As to macro-molecules see H. Staudinger and J. Fritsch, *Helv. Chim. Acta* 1922, 5, 785; *Book*, p. 5.

²⁵ A certain confusion in the field of polymers was caused by an identification between the "micelles" as defined by Nägeli—i.e., small crystallites in the organised fibres, e.g., of cellulose—and the colloid particles in solutions. This identification was repeatedly tried—for instance by R. O. Herzog (*Ber.*, 1925, 58, 1254; *J. Physic. Chem.*, 1926, 30, 457, who assumed that the micelles (crystallites) in cellulose-fibres are of the same size as the micelles (colloid particles) in the colloid solution of cellulose; see discussion of this point in *Book*, p. 31.

of the same kind as those known to be valid in the homologous series of ordinary organic compounds. We may conclude from this that the whole polymeric series, beginning with the hemicolloids and ending with the eu colloids, is built up in the same manner, and differs only in chain-length.

Another proof of the macromolecular structure of high polymers is furnished by the analytical determination of the *end-group* of the thread molecules. But as in the ordinary homologous series, the relative amount of matter belonging to the end-groups of the macro-molecule decreases with its increasing length. Since the length of the macro-molecule is generally very great, this amount is always small; the analytical determination of the end-groups is therefore possible only in some especially favourable cases, and the results are rather inaccurate. Nevertheless with some polymeric series of especially simple structure, it was possible to prove that the relation between the mass of the end-groups and the mass of the whole molecule decreases, conforming with calculations, with increasing order of polymerisation. The substances with which this proof was possible were the poly-oxymethylene dimethyl ether,²⁶ the poly-oxymethylene diacetates,²⁷ and the poly-ethylene-oxide-diactates;²⁸ the end-groups in question were thus the acetyl and the methoxyl group. This method is of course not appropriate for use with very high-molecular eu colloidal products, with a molecular weight of 100,000 and more. It is for instance impossible to determine the molecular weight of cellulose or of caoutchouc by this method.²⁹

The most important proof for the macro-molecular structure of high polymers is their transformation into polymeric-analogous derivatives, that is, into polymers with the same order of polymerisation, but with different substituents. Of course, only substitutions which can be carried out at low temperatures, without unduly affecting the unstabler macro-molecule, can be used for this purpose. The "skeleton" of the macro-molecule is much more sensitive and unstable than that of the ordinary molecules, and the carbon links are the more readily cracked, either by heat or by oxydation, the higher the weight of the molecule.³⁰ This leaves relatively few possibilities of substitutions, at least so far as the relatively stable synthetic high-molecular products are concerned. As an example of substitutions of this kind we may quote the gently catalysed reduction of hemicolloidal polystyrenes, which leads to the polymeric-analogous hydro-polystyrenes of the same order of polymerisation.³¹

TABLE VI. — HYDROGENATION OF POLYSTYRENES TO POLYMERIC-ANALOGOUS POLYHEXAHYDROSTYRENES.

Average Molecular Weight of	
Polystyrene Used.	Polyhexahydro-styrene Obtained
1800	1800
3000	3300
5000	4500

²⁶ H. Staudinger and H. Johner, *Annalen*, 1920, **474**, 205; H. Staudinger and W. Kern, *Book*, p. 224.

²⁷ H. Staudinger and M. Lüthy, *Helv. Chim. Acta*, 1925, **8**, 41; H. Staudinger and R. Signer, *Annalen*, 1920, **474**, 172.

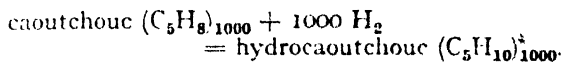
²⁸ H. Staudinger and H. Lohmann, *Book*, p. 298.

²⁹ The end-groups of partially degraded derivatives of cellulose have been determined by W. N. Haworth and H. Machemer, *J. Chem. Soc.*, **132**, 2270; see in this connection H. Staudinger, *Annalen*, 1933, **501**, 170.

³⁰ As to the tearing of thread molecules of polystyrene, see H. Staudinger and W. Heuer, *Ber.*, 1934, **67**, 1159.

³¹ *Ber.*, 1926, **59**, 3033; also H. Staudinger and V. Wiedersheim, *Ber.*, 1928, **62**, 2406.

A much greater variety of possible transformations of this kind can be realised with high-molecular natural products, which are more reactive than the corresponding synthetic substances. It is for instance possible to convert caoutchouc, with a molecular weight of 64,000, composed of 1000 isoprene radicals, into a hydrocaoutchouc with the same length of the molecules.³² This reduction is represented by the formula:



In an analogous way, cellulose can be transformed into polymeric-analogous acetates³³ or nitrates³⁴ without breaking the long chains. The cellulose acetates can be converted back into polymeric-analogous cellulose by saponification;³⁵ or they can be transformed into methyl cellulose³⁶ again without changing the order of polymerisation. It is thus possible to carry out the same transformations with high-molecular substances as with ordinary low-molecular ones; the macro-molecular structure of high polymers is definitely proved in this way.

VII. Determination of the Molecular Weight of High Polymeric Substances.

Since the most important physical properties of the high polymers—their hardness, swelling capacity and the colloidal behaviour of their solutions—depend on the length of their chain-molecules, it becomes very important to determine this length as exactly as possible.

The ordinary cryoscopic or ebullioscopic methods of determination of molecular weight can only be used with hemicolloids (molecular weight up to 10,000), but not with meso- or eucolloids, the corresponding effects being too small in these latter cases. It was, however, possible to use the osmotic method, even in the case of eucolloids, particularly developed by G. V. Schultz in Freiburg; the abnormal osmotic phenomena, which formerly prevented exact investigations of this kind, are now better understood and kept under control.³⁷

Another reliable method for determining particle weights is the ultra-centrifuge, as used by Svedberg. So far it has been used chiefly for determining the molecular weight of proteins.³⁸ Signer and Gross³⁹ used it recently for molecular-weight-determinations of synthetic high polymers, especially those of polystyrene. However, this method is too expensive and complicated to come into general use.

A simple method for calculating the molecular weight (or the chain-length) of high-molecular substances is that based on the measurement of viscosities. It is especially convenient for comparing the different members of a polymeric homologous series.⁴⁰ Experiments of this kind contributed much to the understanding of the constitution of high polymeric substances. Measurements of the specific viscosity of their

³² H. Staudinger and E. O. Leupold, *Ber.*, 1934, **67**, 304.

³³ H. Staudinger and H. Eilers, *Ber.*, 1935, **68**, 1611.

³⁴ H. Staudinger and H. Haas, *Book*, p. 498.

³⁵ H. Staudinger and O. Schweitzer, *Ber.*, 1930, **63**, 3132; H. Staudinger and H. Scholz, *Book*, p. 483.

³⁶ H. Staudinger and H. Scholz, *Ber.*, 1934, **67**, 84.

³⁷ H. Staudinger and G. V. Scholz, *Ber.*, 1935, **68**, 2320. See also Wo. Ostwald, *Kolloid-Z.*, 1929, **49**, 60.

³⁸ Svedberg and Lewis, *Amer. Chem. Soc.*, 1928, **50**, 25; and subsequent papers; see e.g. *Kolloid-Z.*, 1930, **51**, 10.

³⁹ See R. Signer and H. Gross, *Helv. Chim. Acta*, 1934, **17**, 59, 335, 726.

⁴⁰ H. Staudinger and W. Heuer, *Ber.*, 1930, **63**, 222.

solutions under different conditions (variable concentration, variable temperature, different solvents) give valuable hints as to the nature of the colloidal particles involved—especially their micellar or macro-molecular structure.⁴¹ If the macro-molecular structure is established by chemical investigations (as described in the previous section), and the shape of the molecules is known to be thread-like, very simple relations hold between the specific viscosity (at least so far as low-viscous solutions are alone concerned) and the length of the macro-molecules (formula I) or the molecular weight (formula II).⁴²

$$\eta_{sp} (1.4 \text{ per cent.}) = \gamma \times n \quad . \quad . \quad . \quad (I)$$

$$\eta_{sp} (\text{gd. mol.}) = k_m \times M \quad . \quad . \quad . \quad (II)$$

Formula (I) refers to the specific viscosity of the solutions of thread-shaped molecules of constant concentration (1.4 per cent.). It shows this viscosity to be proportional to the number of chain-atoms n . The coefficient γ represents the viscosity-equivalent of a carbon—(or oxygen)—atom in 1.4 per cent. solution. This formula holds for simple thread molecules only, *i.e.*, molecules without rings in the chains. With molecules containing rings, there are some complications, but it still remains possible to calculate n .⁴³

The second formula is obtained by a simple transformation of the first.⁴⁴ It makes possible the direct calculation of the molecular weight M from the specific viscosity of η_{sp} (gd. mol.) of a solution containing one mol. of the monomeric substance (the repeating unit) per litre—provided that the constant K_m is known for the homologous series in question. The validity of these viscosity formulæ has been proved not only on a great number of low-molecular chemical compounds with thread-shaped molecules, but also on a great number of hemicolloids.⁴⁵

The only question is whether these relations hold also for extremely high-molecular substances of eucolloidal character and can be used for calculating the molecular weight of substances of this kind? Since the flow-phenomena in solutions of eucolloids are not normal, it seems doubtful whether viscosity-data can be used for the calculation of molecular weights. But in low-viscous solutions, which alone are used for the determination of the molecular weight, the deviations from the law of Hagen-Poiseuille are so small, that the calculations of η_{sp} (1.4 per cent.) or of η_{sp} (gd. mol.) from the actual measurements of viscosity are not too uncertain.⁴⁶

The usefulness of the viscosity-method for the determination of molecular weight of eucolloids is shown by the fact that, using the results of previous osmotic determinations for cellulose acetates and nitrates,⁴⁷ and combining them with viscosity data we got a value of about 10×10^{-4} for the constant K_m —*i.e.*, the same value as obtained by investigations of the hemicolloids.⁴⁸ The same value was calculated from the viscosities

⁴¹ See Book, p. 96.

⁴² H. Staudinger, *Ber.*, 1932, **65**, 267; *Helv. Chem. acta*, 1932, **15**, 213; Book, p. 56.

⁴³ H. Staudinger and A. Steinhofer, *Annalen*, 1935, **517**, 54; H. Staudinger and F. Staiger, *Annalen*, 1935, **517**, 67. As to the increment of the derivatives of the cellulose, see H. Staudinger and H. Freudenberger, *Annalen*, 1933, **501**, 162; H. Staudinger and E. O. Leupold, *Ber.*, 1934, **67**, 479.

⁴⁴ Book, p. 70.

⁴⁵ H. Staudinger, *Z. Elektrochemie*, 1934, 441.

⁴⁶ See H. Staudinger and W. Heuer, Book, p. 210.

⁴⁷ H. Staudinger, *Ber.*, 1934, **67**, 92. *Ibid.* and Scholz, ref. 37.

⁴⁸ H. Staudinger and H. Freudenberger, Book, p. 466.

of the acetates of cellotetraose⁴⁹ and cellopentaose⁵⁰ prepared by Zechmeister⁵¹—i.e., from well-defined homogeneous compounds. In Freiburg, G. V. Schultz investigated a series of nitrocelluloses and methyl-celluloses and found, that using the value $K_m = 10 \times 10^{-4}$ one obtains values for the molecular weight which are in complete accordance with those calculated by the osmotic method (see Table VII.).

TABLE VII.—COMPARISON BETWEEN THE MOLECULAR WEIGHTS OBTAINED FROM MEASUREMENTS OF VISCOSITY AND OF OSMOTIC PRESSURE.

Substance	$\lim_{c \rightarrow 0} \frac{\eta}{c} \times 10^3$	M (Osmot.)	$\lim_{c \rightarrow 0} \frac{\eta_{sp}}{c}$ g. d.m.	M (Viscos.) with $K_m \times 10^{-4}$	$K_m \times 10^{-4}$ Found
1. Nitro-celluloses in Acetone.					
Prepared from—					
Linters, slightly bleached	0.06	443,000	450	450,000	10.25
Linters, more strongly bleached	0.14	176,000	210	210,000	11.2
Linters, strongly bleached	0.30	81,000	82	82,000	10.1
Viscose-silk	0.48	51,000	50	50,000	11.8
Fractionated product	0.13	189,000	180	180,000	9.5
2. Methyl-cellulose in Water.					
Slightly degraded	0.30	82,000	90	90,000	11.0
Slightly degraded	0.31	79,000	80	80,000	10.15
More strongly degraded	0.50	49,000	50	50,000	11.4
More strongly degraded	0.535	46,000	43	43,000	9.35
3. Poly-ethylene-oxides in Water.					
Catalyst SrCO_3	0.29	94,000	14.1	78,500	1.5
Catalyst CaCO_3	0.275	88,500	10.8	60,000	1.22
Degradation product	0.62	39,300	5.05	28,000	1.29

The validity of the viscosity-law given above is thus demonstrated in a rather wide region, at least for natural high-molecular products, caoutchouc and cellulose.

In the case of synthetic high-polymeric substances, however, the molecular weights obtained by measurement of viscosity often differ from those determined osmotically. In the case of poly-ethylene-oxides G. V. Schultz proved the "viscosimetric" molecular weights to be somewhat lower than those calculated from osmotic experiments. The deviations are, however, not very considerable (see Table VII.).

With polystyrenes, the discrepancies become much larger: the molecular weights determined osmotically are two, three or four times higher than those calculated from viscosity-data (Table VIII.).

The values obtained from *osmotic measurements* are roughly in agreement with those found by R. Signer and H. Gross⁵² with the *ultra centrifuge*.

⁴⁹ H. Staudinger and H. Freudenberger, *Annalen*, 1933, **501**, 162.

⁵⁰ H. Staudinger and E. O. Leupold, *Ber.*, 1934, **67**, 429.

⁵¹ L. Zechmeister and G. Toth, *Ber.*, 1931, **64**, 854.

⁵² See R. Signer and H. Gross, *Helv. chim. acta*, 1934, **17**, 335.

TABLE VIII.—POLYSTYRENES IN TOLUENE (THERMAL POLYMERS).

Temp. of Poly- merisation.	Fraction.	M (Osmot.).	$\lim \frac{\eta_{sp}}{c}$, gm	M (Viscos.) with $K_m = 1.8 \times 10^{-4}$.	$K_m \times 10^4$, Found.	$K_m \times 10^4$, Mean.
20'	I	638,000	79	440,000	1.25	1.22
20'	II	422,000	46	205,000	1.15	
20'	III	193,000	24	133,000	1.25	
60°	I	600,000	50	280,000	0.83	0.79
60°	II	339,000	25	140,000	0.75	
80'	I	516,000	33.2	185,000	0.645	0.607
80'	II	420,000	27.2	151,000	0.655	
80'	III	364,000	20.3	113,000	0.56	
80°	IV	232,000	13.5	75,000	0.58	
135'	I	302,000	15.5	86,000	0.51	0.50
135	II	222,000	10.3	57,000	0.465	
135	III	82,000	4.2	23,500	0.51	
200	I	157,000	6.55	36,500	0.415	0.415

In calculating M from viscosity-data, a value $K_m = 1.8 \times 10^{-4}$ was used, obtained from viscosities of substances whose molecular weight could be measured cryoscopically.⁵³ This experimental value is in good accordance with that obtained from viscosity-measurements on low-molecular compounds of known structure,⁵⁴ which is 1.86×10^{-4} .

The discrepancy between the "osmotic" and the "viscosimetric" values of the molecular weight does not indicate the inexactitude of the viscosity-law in the case of high-molecular polystyrenes. This law is known to be valid in the case of cellulose-derivatives, which are very high-molecular. It is necessary to assume that the synthetic high polymers, produced by chain-reactions, are composed not of simple thread-molecules, but either of high-molecular rings, or of branched chains, formed by some unknown side-reactions. These side-reactions become stronger with rising temperature of polymerisation.

This is the cause of the greater discrepancy between osmotic and viscosimetric determinations of molecular weights in the case of mesocolloidal polystyrenes, obtained by polymerisation at 200°, as compared with higher-molecular euocolloidal products, which are formed at lower temperatures. The discrepancy has nothing to do with an alleged invalidity of the viscosity-laws at higher chain-lengths; otherwise the deviations would be highest in the case of euocolloidal substances, which have the longest molecules. It is, of course, very difficult to prove more

TABLE IX.—COMPARISON OF OSMOTIC MOLECULAR WEIGHTS WITH THOSE DETERMINED BY ULTRACENTRIFUGATION.

Polystyrene.	M (Osmot.).	M (Ultracentrifuge).
Mesocolloid I.	37,000	ca. 35,000
Mesocolloid II.	89,000	80,000

⁵³ H. Staudinger and W. Heuer, *Book*, p. 157.

⁵⁴ *Book*, p. 67. The K_{sp} constant is, according to the latest measurements, 0.93×10^{-4} ; compare H. Staudinger, *Z. Elektrochemie*, 1934, **40**, 441.

directly the existence of branching chains by investigation of the polymerised substances. In a second paper presented to this meeting, we shall demonstrate the strong influence of small amounts of certain foreign bodies upon the straight chain-structure and the properties of high-polymeric substances.⁵⁵

We are led to the following conclusion: whereas osmotic measurements permit the calculation of true molecular weights, viscosity-data give correct results concerning the chain-length. We must bear in mind, however, that the chain-length, and not the molecular weight, is the most important thing from the point of view of the colloidal properties of high-molecular substances.

VIII. Relation between the Physical (Colloidal) Properties of High Polymeric Substances and the Chain-Length of their Molecules.

The most important result of the foregoing discussion can be re-stated as follows: the differences in the colloidal behaviour of high-polymeric substances are based on differences in the lengths of their macro-molecules—and not on different micellar structure, as was hitherto supposed. Synthetic and natural high-polymers with a given chain-length show a characteristic behaviour, irrespective of their molecular structure (for instance, their saturated or unsaturated character). Hydrocarbons, ethers, esters all have the same colloidal properties, so long as their order of polymerisation is the same; the essential colloidal phenomena, especially those of the viscosity of the solutions are mainly dependent on the lengths of the macro-molecules and to some extent on the solvation⁵⁶ and wholly independent on the special chemical structure. The only condition is the purely homœopolar nature of the compound.

It is a well-known fact that many physical properties of low-molecular compounds are primarily functions of their molecular size, e.g., osmotic pressure and volatility. All homœopolar organic compounds with a molecular weight of about 100 are liquids, with about the same boiling-points—whether saturated or unsaturated substances, hydrocarbons, ethers or esters; furthermore they have the same osmotic pressures (when dissolved in the same solvent). Homœopolar organic substances with a molecular weight of about 500 are all much less volatile and possess also about the same boiling-points.

The same connection between molecular size and properties exists also in the range of macro-molecules. Aliphatic hemicolloids with about 200 chain-atoms all have the same appearance—independent of whether they are hemi-colloidal hydrocarbons, or partially degraded hydrocaoutchoucs, or caoutchoucs or poly-isobutylenes, or esters such as poly-acrylic-ester, polyvinyl-acetates. They are all solids, either glue-like or powdery, dissolving without swelling and giving low-viscous solutions. Their specific viscosity in 1.4 per cent. solution is about 0.26 to 0.3 (dependent on the nature of the solvent). Eucolloidal products—caoutchoucs and hydrocaoutchoucs, poly-isobutylenes, polyacrylic esters, etc., with about 5000 chain-atoms, are all tough elastic solids, which swell strongly and form highly viscous solutions. The viscosities of these solutions are about the same for all of these products (so long as solutions in the same solvent and with equal concentrations are compared).

⁵⁵ See the second paper: "The Soluble and Insoluble Polystyrenes."

⁵⁶ H. Staudinger and W. Heuer, *Z. physik. Chemie (A)*, 1934, 171, 129.

The properties of heteropolar substances are essentially different—with low molecular substances as well as high polymers: the properties of sodium acetate are quite different from those of ethyl acetate, although their molecular weights are not very different. In the same way, *the colloidal properties of sodium polyacrylate differ strongly from those of an ester of the polyacrylic acid, even when both have the same chain-length.*

The viscosity of the solutions of heteropolar molecular colloids depends not only on the length of the molecular chains, but also to a high degree on the *formation of swarms between the fibre-ions*. That is why solutions of sodium polyacrylate are much more viscous than those of polymeric-analogous polyacrylic esters with the same chain-length. Due to the formation of swarms, solutions of mesocolloidal heteropolar polymers show deviations from the Hagen-Poiseuille's law, whereas in the case of homœopolar molecular colloids deviations of this kind occur first at a much higher order of polymerisation. Addition of an electrolyte disturbs the electrolytic forces which are responsible for the formation of swarms. The solutions of hetero-polar molecular colloids have therefore different viscosities at different concentrations of electrolytes.⁵⁷ By addition of a large amount of electrolyte, the formation of swarms can be suppressed completely. In this case, the viscosities of heteropolar colloids—for instance of sodium poly-acrylate—obey the same relations which are valid for homœopolar polymers. Under these conditions, the viscosity depends only on the length of the chain-ions and on their solvation. This discovery has contributed much towards the understanding of the structure of heteropolar molecular colloids.⁵⁸

IX. Classification of Colloids, Based on the Structure of High-Molecular Polymers.

It is well known that the characteristic differences between the behaviour of a solution of glue and that of ordinary solutions of low-molecular substances brought Graham to the notion of a special state of dissolved matter known as the colloidal state. The number of colloidal substances now known is very large, and between them great differences in properties can be observed. These differences lead to a discrimination between two chief classes of colloids: the *lyophilic* and the *lyophobic* colloids.⁵⁹ This classification is based on the assumption that the swelling of certain solid substances which give colloid solutions, and the high viscosity of these solutions, are based on an especially strong solvation of the colloid particles in question. Other authors prefer to discriminate between *suspenseoids* (grain-colloids) and *emulsoids* (drop-colloids), assuming a different state of aggregation of the colloid particles in these two cases. The high-molecular substances belong to lyophilic colloids according to the first, or to the emulsoids according to the second classification. Nowadays, since investigation of the structure and size of the colloid particles of high-molecular substances has led to definite results, a further classification of the colloids appears reasonable.⁶⁰

Neglecting the inorganic colloids, whose structure may be very different, we can divide all organic colloids into two classes: the *micellar* and the *molecular* colloids.

⁵⁷ H. Staudinger and E. Trommsdorff, *Book*, p. 333.

⁵⁸ H. Staudinger and E. Trommsdorff, *Annalen*, 1933, **502**, 201.

⁵⁹ H. Freundlich, " *Kapillarchemie*," 4th edition, Vol. II., pp. 2 and 3 (1932).

⁶⁰ As to the classification of colloids, see *Ber.*, 1935, **68**, 1682.

We have shown in this paper, how differences in the shapes of the colloidal particles affect the properties of their solutions. This causes us to distinguish between *sphero-colloids* and *linear colloids* (or *thread-colloids*).⁶¹

A. Sphero-Colloids.—Colloids of this kind can never produce solutions of high viscosity, since from Einstein's formula: $\eta_{sp} = 2.5\phi$ we calculate that a solution containing 1 volume in 100 of spherical colloidal particles must have a viscosity of not more than 0.025. This value is to be compared with the high viscosities (up to $\eta_{sp} = 10$, or even 100), which are actually shown by 1 per cent solutions of many lyophilic colloids. The solutions of the sphero-colloids obey the Hagen-Poiseuille law. No swelling occurs during their dissolution.

B. Linear Colloids.—These colloids produce highly-viscous solutions, because the viscosity of a solution containing long, fibre-shaped particles depends on the size of the fibres (whereas in the case of spherical colloids the viscosity is independent of the size of the particles). At a given concentration, the viscosity increases strongly with increasing length of the colloidal particles. This applies to the micellar colloids (e.g., soaps), as well as those with fibre-shaped macro-molecules, and their solutions.

The high viscosity of the solutions of rod-shaped particles can be explained by assuming a great size of their "spheres of action." It is therefore possible to prepare a solution of linear particles in which each particle is completely solvated—and still remains in interaction with the neighbouring molecules (or micelles).⁶² The viscosity of gel-solutions⁶³ of this kind may attain extremely high values—some high-molecular substances give solutions with viscosities a 100 times greater than that of the pure solvent. *This is characteristic for linear colloids; it would never occur with sphero-colloids.*

Solutions of linear colloids show deviations from the Hagen and Poiseuille law, which become greater with growing length of the particles.⁶⁴ Solid linear colloids are dissolved with strong swelling, which becomes especially intense with the longer particles.⁶⁵

The difference in the colloidal behaviour of the two classes can be further demonstrated by the following example. By polymerising unsaturated compounds—for instance, styrene—in a solution of soap, it is possible nowadays to prepare an artificial latex, whose internal structure does not greatly differ from that of the natural product.⁶⁶ The polystyrene-latex and natural latex both contain spherical particles. By changing the conditions, it is possible to obtain particles of different size, and polystyrenes with a different order of polymerisation.⁶⁷

⁶¹ Molecular colloids may be sphero-colloids, but are usually linear colloids. Molecular colloids, with spherical particles, have been so far observed with proteins only; Svedberg and N. Lewis, *J. Amer. Chem. Soc.*, 1928, **50**, 525, and subsequent papers; G. Boehm and R. Signer, *Helv. chim. acta*, 1931, **14**, 1370. A synthetic preparation of a spherical colloid remains yet to be achieved; by polymerisation of unsaturated compounds so far only linear colloids have been obtained.

⁶² H. Staudinger and W. Heuer, *Z. physik. Chemie (A)*, 1934, **171**, 176.

⁶³ H. Staudinger, *Trans. Faraday Soc.*, 1933, **29**, 29.

⁶⁴ H. Staudinger and H. Machemer, *Ber.*, 1929, **62**, 2924; H. Staudinger and W. Heuer, *Book*, p. 191.

⁶⁵ H. Staudinger, *Kolloid. Z.*, 1931, **54**, 135; *Book*, p. 138.

⁶⁶ J. G. Farbenindustrie, B.P. 307,930 and Br. Fr. 709,592.

⁶⁷ See the forthcoming paper by H. Staudinger and E. Husemann, *Ber.*, 1935, **68**, 1631.

The emulsions of latex are sphero-colloidal solutions, having, therefore, a low specific viscosity (0.025 at a concentration of 1 per cent.), independent of the size of the latex-drops and of the macromolecules of polystyrene from which these drops are built up. These results are confirmed by the investigations of Bancelin⁶⁸ on rubber suspensions.

The polystyrene can be precipitated from the synthetic latex by the same substances which precipitate rubber from rubber-latex, e.g., acetic acid or acetone. By dis-

TABLE X.—COMPARISON BETWEEN THE SPECIFIC VISCOSITIES OF 1 PER CENT. SOLUTIONS OF POLYSTYRENE-LATEX AND OF POLYSTYRENE IN BENZENE.

(After experiments by E. Husemann.)

		Molecular Weight of Polystyrene.	η_{sp} (1 Per Cent.) of the Latex.	η_{sp} (1 Per Cent.) of the Polystyrene Solution.
Latex I		750,000	0.027	180.0
" II		400,000	0.028	32.6
" III		275,000	0.024	10.5
" IV		175,000	0.026	5.6

solving the precipitated polystyrene in benzene, we obtain highly viscous solutions of a linear-colloidal type. Table X. gives a comparison between the viscosities of a

1 per cent. solution of polystyrene-latex and a polystyrene-solution of the same concentration. The relation is sometimes as high as 1000; it is seen that the viscosities of the polystyrene solutions change strongly with the length of the molecules.

GENERAL DISCUSSION.

Dr. R. Houwink (*Eindhoven*) said: I suggest that the view that polycondensations do not yield eucolloidal products must be restricted to linear polymers. 1 or three-dimensional polymers the phenol-formaldehyde resins are a proof of the contrary. I would like to know how the low viscosity of a polystyrene latex can be brought into accordance with the rigidity of the polystyrene chain molecules, which has often been defended by Professor Staudinger.

Professor K. H. Meyer (*Genève*) said: Dr. Staudinger says, in Chapter VI. of his paper, that there was much discussion as to whether substances such as cellulose are built up from macromolecules or from micelles. We think that this alternative is not justified. Cellulose is built up from long chains, the length of which was determined (by a Roentgenographical method) by Mark and myself⁶⁹ as early as 1928 to correspond to at least 100 glucose residues,^{70a} which is in harmony with the

⁶⁸ Bancelin, *Comptes rendus*, 1911, **152**, 1382.

⁶⁹ *Z. physik. Chem.*, 1928, **2B**, 128.

^{70a} The first preliminary value of 30-50 glucose residues, quoted several times by Staudinger, was replaced in 1928 by the value of "at least 100 residues, held together by cellobiose linkages," which resulted from our own measurements. At this time Staudinger's views on the structure of cellulose were still quite undefined; he wrote (*Ann.*, 1929, **474**, 150); *Bei der Cellulose ist die Frage noch offen, ob die einzelnen Moleküle wie Glukose-, bzw. Cellobioseanhydrid-Moleküle durch normale oder durch koordinative Covalenzen gebunden sind.*

recent work of Haworth,⁷⁰ who finds 200 rings in a chain. These chains in the natural, and any solid state are clustered together to crystalline aggregates, called micelles. Staudinger's alternative is expressed as if one were to discuss whether a house is built up of bricks or of walls.

Staudinger considers the chemical transformation of high polymeric substances into polymeric analogous substances (e.g., polystyrene into hypopolystyrene of the same particle size) as the most important proof for their macromolecular structure and against the existence of micelles or aggregates in solution. We do not think that this argument is conclusive. Oleic acid is bimolecular in apolar solvents, and forms polymolecular micelles in aqueous alkaline solution. If we hydrogenate it, we get stearic acid, which forms double molecules or ionic micelles of about the same particle size as oleic acid. Other acids will give analogous results, and show other characteristic particle sizes. According to Staudinger, this would be a definite proof of the "macromolecular structure," and the absence of micelles in these compounds. But in our opinion real physical (e.g. Roentgens graphical) and chemical arguments exist in favour of very long primary valency-chains (in cellulose, rubber, etc.).⁷¹

On the other hand, there is, as Haworth has pointed out, and Rideal mentioned in his introductory paper, very much evidence in favour of the assumption that, in solution, the particles of cellulose and other substances with dipoles are composed of several primary valency-chains. The same opinion has been expressed by us, but we have never admitted, as Staudinger seems to interpret our views, that the crystalline micelles of the natural cellulose persist in the same state in the solution. On the contrary, we emphasised that intramicellar swelling precedes the dissolution.

Professor H. Pringsheim (Paris) said: I have observed that by heating inulin, even in aqueous solution, can be transformed into a substance which is easily soluble in water. I have called this substance "Inulan" while Dr. Katz prefers to call it "soluble inulin". This substance if left for a certain length of time in a dessicator will change back into the original inulin with the original chemical qualities: the same difficult solubility in water and the same X-ray diagram. I cannot see how this can be explained on the basis of the theories here accepted for the constitution of high-polymer polysaccharides and I would like to ask whether anybody here present could give me an explanation.

Professor H. I. Waterman (Delft) said: Does Professor Staudinger not agree that the conclusion: "unsaturated compounds with conjugated double bonds are generally more reactive than those with isolated double bonds" will have many exceptions? It is known from experiments in

the Delft laboratory that the isobutene $\left[\begin{array}{c} \text{C} \\ | \\ \text{C} \quad \text{C} \end{array} \right]$ polymerisation even at -80°C ., has an explosive character.

In the reaction "caoutchouc/ $\text{C}_5\text{H}_8/1000 \rightarrow 1000\text{H}_2$ Hydrocaoutchouc/ $\text{C}_5\text{H}_{1000}$ " was it proved that (a) the raw material which is hydrogenated is absolutely free from rings, and (b) there is no cracking or ring formation during the hydrogenation?

⁷⁰ *Pres. Address, Sect. Chemistry, Brit. Assoc., 1935.*

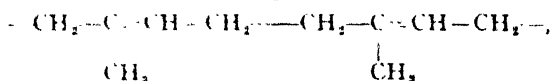
⁷¹ It seems to have been forgotten that the macromolecular cellobiose formula of cellulose was proposed long ago with very strong arguments by different authors, e.g., Jacobson in the *Lehrbuch der organischen Chemie* (Meyer-Jakobson, 2nd ed., 1913), who says: *Wir können aus der Gesamtheit der Eigenschaften (der Polysaccharide) schliessen, dass es sich um Körper von sehr hohem Molekulargewicht handelt. . . . In einzelnen Fällen gelingt es, durch gemässigte Hydrolyse Disaccharide abzuspalten (Maltose aus Stärke, Cellobiose aus Cellulose). Man darf dann schliessen, dass die in diesen Disacchariden sich findende Verkettingsart je zweier Monosaccharidereste auch dem molekularen Aufbau des komplexen Polysaccharids zugrunde liegt.*

In my opinion a cracking reaction cannot generally be accepted as a proof of the constitution of styrene polymers. The cracking reaction was indeed proposed by Professor Staudinger during the discussion on de Boer's paper as an argument for a special constitution. I believe that this can give rise to mistakes, unless it is proved in another way that the decomposition in cracking is not combined with side-reactions, *e.g.*, polymerisation.

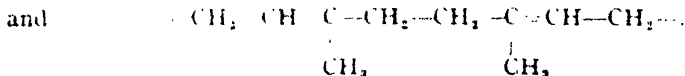
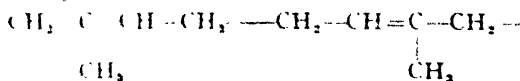
Dr. E. Bergmann (*Rehoboth*) said: (1) One cannot divide the polymerisable substances into two classes: substances polymerising spontaneously and substances polymerised under the influence of catalysts. Indene, *e.g.*, on keeping, polymerises easily, whilst according to Professor Staudinger's statement a catalyst is necessary. If one considers polymerisation as a chain reaction, even on theoretical reasons the above discrimination cannot be maintained, since the chain needs a starter catalyst.

(2) The statement that negative groups, such as phenyl or chlorine, increase the polymerisability of ethylene compounds, applies only for the pair ethylene-styrene, whilst in the case of butadiene-phenylbutadiene the reverse is true. The careful study of the influence of substituents may give, from the chemical side, an insight into the nature of the "steric factor," concerned in the polymerisations, as has been discussed already with regard to previous papers.

(3) Regarding the constitutional regularity of the polymerisation process, a paper by Midgley and Henne may be quoted; they showed that the dimerisation of isoprene with sodium metal in presence of hydrogen gives not only the dimerisation corresponding to natural rubber



but also the following chains:



The conclusion is obvious that if the same applies to the polymerisation process, the regularity necessary for giving an X-ray pattern will not be reached, and that may account for the failure to obtain X-ray diagrams from artificial polyisoprene.

Professor H. Mark (*Wien*) said: For everybody who seeks to study the kinetics of polymerisation reactions Table I. of Staudinger's contribution is of the greatest importance. It will be the main task of physical measurements and of calculations, which are based on these measurements, to explain why several substances polymerise with difficulty, whilst other very similar substances polymerise easily. It seems to me that the idea of chain reactions, which has already been pointed out by different authors (as mentioned by Professor Rideal in his introductory paper) and which Dr. Dostal and I have worked out to a certain extent, furnishes a sufficient number of possibilities of explaining the complicated experimental behaviour.

That ethylene does not polymerise may be understood from the fact that the double bond in this molecule is activated only at somewhat high temperatures, at which the chains formed by this activation disintegrate again with a remarkable velocity. This means, that nuclei are only built with appreciable rate at temperatures, which are so high that the resulting product is already unstable. On the other hand, it was found possible to polymerise ethylene together with styrene or vinyl chloride. This is due to the fact that the radicals, which induce the polymerisation of

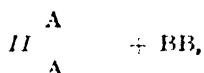
styrene are sufficiently active to induce also the polymerisation of ethylene. That polymerising substances may induce other substances to polymerise with them has a certain analogy to similar effects in explosions and is characteristic for the occurrence of a chain reaction. The large amount of material contained in the numerous publications of Professor Staudinger furnishes a great number of valuable points of view for the quantitative analysis of polymerisation reactions.

The fact that condensations and especially esterifications mostly lead only to hemicolloid molecules of medium chain-length can very easily be understood from the standpoint of a chain reaction. In these cases the rate of the first step of the polymerisation which leads from A_1 to A_2 is, in regard to its activation energy, identical with every step which leads from A_n to A_{n+1} . In all cases one has to deal with the splitting-off of water, by which an ester is built. An activated state or a free radical is not to be taken in account. Therefore one sees no reason why, after a slow chain production, a rapid chain growth should begin. One has simply a reaction of stepwise esterification, which slowly builds up the macromolecules. At the same time new molecules A_2 , A_3 , etc., are always formed and together with the slowly growing chains to form the monomeric material. The formulae which we have derived in our contribution make it possible to follow this behaviour quantitatively.

Dr. J. H. de Boer (*Eindhoven*) said: It may be assumed that some thread-like polymers have a stretched form in some liquids in which they are solvated to a high degree, while the same polymers will have a spiral form in other liquids which are not bound by solvation forces. When a chain has the property of giving a spiral form by the working of the van der Waals' forces along the chain, one may expect this in the first place in the dilute gaseous state. When brought into a liquid, there are two possibilities. Suppose we have a polymer molecule $A \dots A$ and two molecules of some liquid B, we may distinguish the combinations



in which each A-group has bound a molecule B by van der Waals' forces, and



in which the A-groups attract each other and the molecules B do the same. In case I. we have the van der Waals' binding energy

$$Q_I = 2 \cdot \frac{3}{2} \alpha_A \alpha_B \frac{h\nu_A \nu_B}{\nu_A + \nu_B} \approx \frac{1}{\nu_A},$$

whereas we have in case II:

$$Q_{II} = \frac{3}{2} \alpha_A^2 h\nu_A \approx \frac{1}{\nu_A^2} + \frac{3}{2} \alpha_B^2 h\nu_B \approx \frac{1}{\nu_B^2}.$$

When $\nu_A = \nu_B$ and $\alpha_A = \alpha_B$, so when the dispersion liquid has about the same physical properties as the groups of the polymer,

$$Q_I = Q_{II}.$$

On account of, let us say, steric factors, we may expect that the A-A-attraction is smaller than it would be when the A-groups were entirely free, so

$$Q_I < Q_{II},$$

and there will be a great solvation and a tendency to form stretched molecules in this liquid.

When, however, $\nu_A \neq \nu_B$ and $\alpha_A \neq \alpha_B$, as when the molecules of the liquid have entirely other physical properties than the groups of the polymer, then

$$Q_I < Q_{II},$$

and there may be a tendency to form spirals, and the solvation is small.

This behaviour seems to me to be in accordance with the results of Professor Signer,⁷² where he states that there is a large double refraction of flow in the case of polystyrene, dissolved in benzene, toluene or the like, but that in other liquids the double refraction of flow has much smaller values and the molecules of polystyrene have not a stretched form. This latter behaviour may be expected to a higher degree, the greater the difference between the molecules of the liquid and the groups of the polymer.

Dr. E. W. Fawcett (*Winnington*) said: In connection with Professor Staudinger's remarks on the relative ease of polymerisation of various unsaturated compounds, I should like to report some preliminary results on the polymerisation of ethylene under high pressures. The polymerisation of ethylene when carried out at ordinary or moderately high pressures with or without the addition of catalysts, does not usually lead to the production of products of very high molecular weight—the products generally being liquids of molecular weight of the order of 100-500. When, however, ethylene is heated to 170° C. under a pressure of about 1000 atms., a slow polymerisation occurs leading to the production of a white solid polymer. This is insoluble in acetone, and moderately soluble in benzene, has a carbon and hydrogen content corresponding to the formula $(CH_2)_n$, and a molecular weight by boiling-point elevation in benzene of about 1000. In spite of the fact that the reaction was by no means complete—only about 10 per cent. of the ethylene had reacted—no liquid products of low molecular weight were produced, and the reaction appears to be quite analogous to the well-known chain polymerisation of styrene and similar substances. When an attempt was made to carry out the reaction at a pressure greater than 1400 atms., a very violent exothermic reaction occurred with the production of carbon, hydrogen and simple hydrocarbons.

Professor H. Staudinger (*Leipzig 1. Br.*), in reply, said: I will take those questions together which cover a similar field. In regard to the questions of Waterman, Bergmann, Mark, and Fawcett, it should be pointed out (as H. Mark has already stated), that Table I. of my paper is only of a qualitative nature in order to direct attention to the multiplicity of the phenomena. Naturally, it is very difficult to decide whether an unsaturated substance polymerises with or without a catalyst, because traces of impurities, *e.g.*, peroxides, can accelerate the polymerisation catalytically. It may be observed that ordinary vinyl acetate, when heated to 100-120°, polymerises within a few days. When air is carefully eliminated a sample can be heated for several months without polymerisation taking place.⁷³ Therefore numerous investigations will be required in order to supplement the qualitative facts with quantitative data. Certainly the work at present being carried out by Rudeal and his collaborators, by Mark and others, will contribute much to increase our knowledge in this direction, which is also of great importance to industrial chemistry.

An explosion-like course of the polymerisation was repeatedly observed in the cases of the polymerisation of monomeric formaldehyde, of acrylic esters and ethylene oxides. The reason for this is that these polymerisations are strongly exothermic reactions. On account of this large development of heat the more volatile compounds evaporate to a large extent, giving rise to very high vapour pressures.⁷⁴

In my paper I mentioned that very high molecular weight products can arise only by the peculiar chain polymerisation process, but not by polycondensation reactions. As Mr. Houwink correctly remarks, this statement holds only for linear macromolecules but not for three-dimensional macromolecules. In the phenol formaldehyde polycondensation reaction

⁷² This vol., p. 296.

⁷³ H. Staudinger and A. Schwalbach, *Lieb. Ann.*, 1931, **488**, 32.

⁷⁴ Compare H. Staudinger and O. Schweitzer, *Ber.*, 1929, **62**, 2307.

very large three-dimensional macromolecules can be formed. On the other hand, it is very unlikely that linear high molecular weight products of eucolloidal character can be built up by polycondensation processes, because in this case the number of reactive parts of the molecules is comparatively small, as H. Mark has also pointed out.

In regard to the question of Professor Waterman as to the transformation of caoutchouc into hydrocaoutchouc I have to remark that the catalytic hydrogenation is carried out with very dilute solutions, a condition under which cyclisation cannot occur. In addition a series of polymeric homologous caoutchoucs of different average molecular weights was transformed into the polymeric analogous hydrocaoutchoucs, which thus is a proof of the macromolecular structure of caoutchouc.⁷⁵

In regard to the remarks of Dr. de Boer, it would, of course, be very interesting if one and the same macromolecule could exist in one case as a linear colloid, and in another as a sphero-colloid. In homopolar solvents polystyrene molecules are linear colloids. It is possible to imagine in a heteropolar solvent that a thread molecule could roll up, thus assuming a sphere-like form, since in this case only weak van der Waals' forces exist between the solvent and the dissolved substance. However, experiments in this direction have not yet proved successful. In the polystyrene latex the colloid particles are not single molecules of polystyrene rolled up in the form of spheres, but a single latex drop has approximately spherical shape and is estimated to contain 10^6 - 10^9 single molecules forming one micelle.

I regret that Professor Kurt Meyer⁷⁶ once more brings forward a question which I consider to have been completely answered long ago by the discussions of recent years. K. H. Meyer is of the opinion that the macromolecular nature of high molecular weight compounds is not definitely proved by their transformation into polymeric analogous products, and he quotes, e.g., that in the transformation of a soap micelle into fatty acid esters and also in the transition of a fatty acid into its derivatives a change of the particles occurs. To this I can only point out that the proof of the macromolecular structure of synthetic as well as natural high molecular weight compounds, such as rubber and cellulose, depends not upon a single but upon numerous reactions giving results that agree well with each other.⁷⁷

Numerous series of polymeric homologous products have been prepared, and the change of physical properties with molecular weight has been carefully investigated. Since these changes take place in a strictly regular manner, one is entitled to draw the conclusion that high molecular and low molecular weight compounds possess a similar structure. According to this, the end members of a polymeric homologous series (e.g., of rubber and cellulose) have the same molecular structure as the members at the beginning of the series. Their structure is a macromolecular one and not a micellar one. Hence, in addition, the transformation of various members

⁷⁵ Compare H. Staudinger and E. O. Leopold, *Ber.*, 1934, **67**, 304.

⁷⁶ In footnote ^{70a} K. H. Meyer quotes from *Annalen* 1929, but he does not add that in this very publication, on pp. 259-271, detailed reasons were put forward to show that, based on experiments with the polyoxymethylenes, a macromolecular structure must also be assumed in the case of cellulose. This assumption was often made in times gone by, but in the past 10 years it has frequently been rejected, especially by X-ray workers. The macromolecular structure of cellulose was finally proved by the preparation of polymeric homologous series and their transformation into polymeric analogous products* and moreover, the molecular weight of the cellulose molecule was determined by viscosity measurements. The earlier hypotheses of K. H. Meyer as to the size of the cellulose molecule, which he quotes, have never been put on a sufficiently sound experimental basis.

* Compare H. Staudinger, *Naturwissenschaften*, 1934, **22**, 797 and *Trans. Faraday Soc.*, 1933, **29**, 18.

⁷⁷ Compare H. Staudinger, *Die hochmolekularen organischen Verbindungen, Kautschuk und Cellulose*, Springer, 1932.

of one polymeric homologous series into the corresponding polymeric analogous products shows that in the case of the high molecular weight products analogous chemical transformations can be carried out, as can be done with compounds of low molecular weight.

Furthermore, K. H. Meyer points out that the opinion set forth in my publications is not in contradiction to his, since solid crystalline cellulose is built up of micelles which, also, in his opinion, are split into single molecules when brought into solution. I must remind Professor Meyer of his earlier publications of 1928,⁷⁸ in which the hypothesis was set forth that, in analogy with the ideas of R. O. Herzog,⁷⁹ the micelles in a solution and in the solid state were said to have a similar size. Such a micelle was supposed to be built up of 40-60 primary valency chains, each chain containing 30-50 glucose residues.⁸⁰ This conception was generalised and such a micellar structure was put forward as applicable to all high molecular weight compounds. The colloidal properties of their solutions were thought to be dependent on the micellar structure of the colloid particles. In contradiction to this, I have furnished proof that the colloidal particles of a dilute solution of cellulose and its derivatives just as in the case of the solutions of synthetic high polymers are identical with the macromolecules themselves, and that the colloidal properties of these solutions, especially their high viscosity, do not depend on the micellar structure of the particles, but upon the fact that they are built up of long thread molecules. To give a parallel, the difference between the two conceptions may be presented as follows: a micelle, according to K. H. Meyer, is represented by a series of short rods collected into a bundle similar to matches in a box. A macromolecule, on the other hand, is to be compared with a very long thin rod, 500 to 1000 times longer than it is thick.

In this connection, I should like to discuss the remark of Professor Pringsheim with regard to the constitution of inulin. Although unable to answer his question, since investigations on inulin have not yet been carried out in the Freiburg laboratories, I want to point out that the evidence obtained for the macromolecular structure of cellulose cannot be directly applied to prove a macromolecular structure of inulin. Moreover, it will be necessary to elucidate also in this case the structure and size of the molecules according to the methods of organic chemistry before relationships between the physical properties and the constitution of the molecules can be obtained; only when this has been established can Dr. Pringsheim's question be answered.

I would like to emphasise the fact that in the field of the high molecular weight compounds the same outlook should be adopted as for the low molecular weight compounds: therefore, it must be clearly realised *that the physical and chemical properties of high molecular weight substances depend upon the structure and the size of their macromolecules, and not upon a type of micellar structure*, as has been previously suggested by K. H. Meyer and many colloid chemists.

In conclusion, I may draw attention to the following interesting remarks of K. H. Meyer⁸¹ which characterise clearly his earlier point of view on the colloid particles of solutions of high polymers: "It is unsuitable to designate as molecules the units which we designate as main valency chains and which possess different chain lengths; for their average size cannot be determined by the osmotic methods of molecular weight determinations, moreover these furnish the weight of a micelle composed of many main valency chains."

⁷⁸ *Z. angew. Chem.*, 1928, **41**, 935.

⁷⁹ R. O. Herzog, *Ber.*, 1925, **58**, 1254.

⁸⁰ K. H. Meyer and H. Mark, *Ber.*, 1928, **61**, 595.

⁸¹ *Z. angew. Chemie*, 1928, **41**, 946.

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into the strength of the internal bonds of a material, a problem of great importance for high polymers.

Taking into account the attractive and repulsive forces F between two atoms 1 and 2 of a material, the interatomic distance a will be as shown in Fig. 1.

In order to remove atom 2 from the sphere of attraction of atom 1, an attractive force must be overcome. When the distance has been increased by an amount $a' - a$, the attractive force reaches a maximum F_m after which the force decreases again. One may therefore say that $a' - a$ corresponds to the elongation ϵ when the yield value is reached. F_m represents the rupture strength per pair of atoms.

As follows from an article by de Boer,² the modulus of elasticity of the bond between atoms 1 and 2 is represented by the distance E , when no account is given to Poisson's Ratio.

The rupture energy e_r for this pair of atoms can now be calculated as

$$e_r = - \int_a^{\infty} F dx \quad . \quad . \quad . \quad (2)$$

and is represented by the cross-hatched area in Fig. 1.

For the aliphatic C—C bond, which is of special interest in our problems, $e_r = 6.95$ electron volts (160 kg. cal. per gram equivalent), cf. de Boer.²

§ 2. Theories about the Internal Structure of Asphalts, Resins and Glass.

The amorphous materials may be divided into two groups, namely, one in which the structural units (or groups of these units) cohere by means of primary bonds, and one in which the coherence is effected by means of secondary bonds (by van der Waals' forces, for example). There is a great difference in energy content between these two kinds of bonds (cf. the paper presented to the present discussion by J. H. de Boer², and it is one of our purposes to deal with the elastic properties of the amorphous materials on the basis of that energy difference. For this reason it is necessary to point out briefly the part played by the different bonds in the formation of the substances under discussion.

² J. H. de Boer, *Trans. Faraday Soc.*, this volume. Dr. de Boer remarked in a discussion that one cannot assume merely from Fig. 1 that a large energy content will always result in a large modulus E . To understand this relation one has to consider that a large energy content will result in a small interatomic distance a and, as a consequence of this, the tangent in 2 will be steeper.

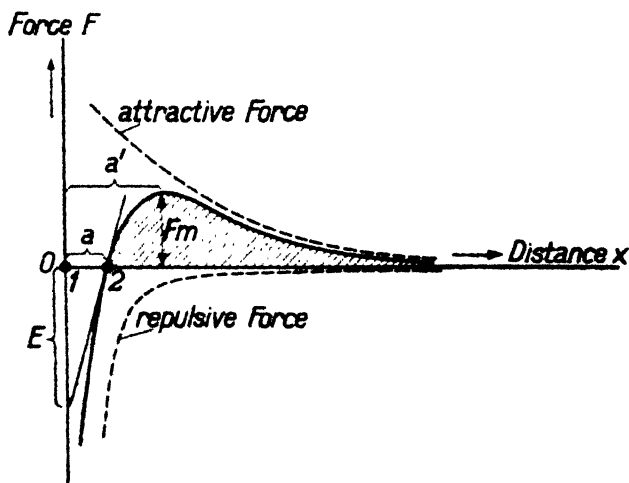


FIG. 1.—Diagrammatic representation of the Forces between two atoms 1 and 2.

(1) In the case of *asphalts*, asphaltenes are assumed to be present, in which the coherence is probably effected by primary bonds,³ together with petrolenes,⁴ which consist of asphaltic resins and oily constituents bound to each other and to the asphaltenes by means of secondary bonds. The so-called steam refined asphalts contain roughly 20 per cent. of asphaltenes, and this content may be increased by means of oxidation (combined with a destructive distillation) to about 30 per cent. such as is encountered in many of the so-called blown asphalts.

(2) The case with *resins* (only the three-dimensionally polymerising resins are considered here) is much more complicated. The author⁵ has already described in full how one may assume non-crystalline micelles to be present in a non-hardening resin and in the fusible (and soluble) *A* stage of a hardening resin as well. These micelles are assumed to cohere by means of secondary bonds. These bonds may be compared with those in asphalts. The case of the hardening resins is different from that of the non-hardening resins in so far as in the hardening resins reactive spots are supposed to be present on the surface of the micelles which enable the micelles to react with each other. As a consequence of the resulting growth of the micelles the resin passes from its (assumed) isogel state through the *B* stage (somewhat fusible and only partly soluble, still an isogel) into the infusible *C* stage. Since this resinification will be dealt with in detail later, a scheme which probably represents the chief reaction⁶ is reproduced in Fig. 2.

According to this scheme only primary bonds would be present in the macromolecule formed. We shall see in how far the data concerning mechanical properties support this conception. In the following discussion the resins in the *A*, *B* and *C* states will often be denoted as *A*, *B* and *C* resins respectively.

(3) The most detailed description of *glass* has been given by Tammann.⁷ According to this author, during the cooling of a liquid glass, when a certain temperature T_g is reached, the freely rotating molecules begin to cohere to form larger units (gel or isogel state; compare note 5). At a second (lower) temperature T_0 this coherence should be complete so that below T_0 no freely rotating molecules should be present. The region between T_g and T_0 is usually called the *transformation interval* and corresponds to a viscosity of about 10^{13} poises. Tammann obviously assumes primary bonds to be present in the molecules. In the temperature interval from T_g to T_0 the formation of secondary bonds between the molecules is accepted by some authors.⁸ Another opinion, somewhat contradictory to the above, is that of Zachariassen,⁹ who assumes for certain kinds of glass a coherence of ions (called atoms by him, as is often

³ F. J. Nellensteyn, footnote 1.

⁴ C. Mack, *Proc. of techn. Session Assoc. of Asphalt Techn.*, Dec., 1933, 11. Mack, *J. Phys. Chem.*, 1932, **36**, 2901.

⁵ R. Houwink, *Physikalische Eigenschaften und Feinbau von Natur- und Kunstharzen*, Leipzig, 1934.

⁶ There are other opinions about the reaction scheme. In so far, however, as they also assume a molecular growth by means of primary bonds, our general considerations to be developed in this paper, *mutatis mutandis*, will remain the same. In addition, secondary reactions will of course also take place.

⁷ G. Tammann, *Der Glaszustand*, Leipzig, 1933.

⁸ See for a survey of the problem, E. Berger, *Z. techn. Physik*, 1934, **15**, 443. In this survey Berger assumes both "chemical" bonds and "physical" bonds to play a rôle.

⁹ W. H. Zachariassen, *J. Amer. Chem. Soc.*, 1932, **54**, 3841; *J. Chem. Physics*, 1935, **3**, 162.

done in crystallography) which is of course effected by primary bonds. A more general theory of glass-formation was given by Hägg¹⁰ who in some cases introduces two kinds of primary bonds, homopolar and heteropolar. Without deciding between these two last-mentioned theories, we may, however, fully accept the assumption made by both in regard to the rôle of primary bonds in glass formation. The high softening temperature is the best proof of the great energy content of these bonds.

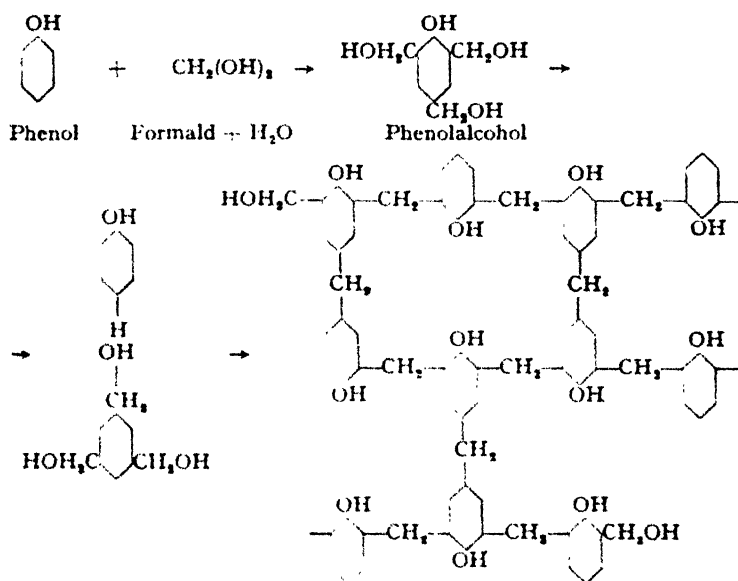


FIG. 2.—Condensation of phenol formaldehyde resin.

This representation is very diagrammatic. The benzene nuclei must be imagined to be linked in three dimensions, but not in a regular manner, so that there is no question of a crystalline pattern. This has been proved by means of X-ray measurements by W. G. Burgers and R. Houwink.⁸

From this point of view a great similarity must be expected between the mechanical properties of a C resin and those of glass. In order to make the comparison the following energy contents may be mentioned. For a C phenol-formaldehyde resin the C—C bonds may be assumed to have an energy content of about 160 kg. cal. per gram equivalent (see above). For glass one may assume an order of magnitude of about 200 kg. cal. for the alkali ions in an alkali glass. This value increases with decreasing alkali content. On this basis very high values for Young's modulus and tensile strength may be expected in both cases; these quantities will be of a different order of magnitude from those for asphalts and non-hardening resins, where secondary bonds predominate.

§ 3. Observations on the Modulus of Elasticity and Strength of Asphalts, Resins and Glass.

In Table I. some figures (taken partly from the literature) have been tabulated for the modulus of elasticity and the tensile strength of the materials under discussion as well as of some other materials for comparison. In some cases values at the temperature of liquid air ($-195^{\circ}\text{C}.$)

¹⁰ G. Hägg, *J. Chem. Physics*, 1935, 3, 42.

have been added, since at this temperature plastic deformations are practically excluded, a fact which is uncertain at room temperature. More-

TABLE I.—MODULUS OF ELASTICITY AND TENSILE STRENGTH OF ASPHALTS, RESINS¹¹ AND GLASS COMPARED WITH OTHER MATERIALS.

	Modulus of Elasticity <i>E</i> in kg. mm. ⁻²		Tensile Strength <i>F</i> in kg. mm. ⁻²		Elongation at Proportional Limit <i>e</i> in Per Cent.	
	At 20° C.	At -195° C.	At 20° C.	At -195° C.	At 20° C.	At -195° C.
<i>Asphalts.</i>						
Asphalt ¹² (various grades)	100-200	—	$3-82 \times 10^{-2}$	—	—	—
<i>Resins.</i>						
Colophony	200	—	$\pm 1 \times 10^{-2}$	—	—	—
Cresol-formald. :						
A stage	152	—	$\pm 1 \times 10^{-2}$	—	—	—
Moulded 10 min./						
150° C. (C stage)	513	—	2.5	—	—	—
Moulded 60 min./						
150° C. (C stage)	500	503	3.3	3.5	0.6	0.5
Phenol-formald. :						
A stage	200	—	$\pm 1 \times 10^{-2}$	—	—	—
Moulded 10 min./						
150° C. (C stage)	501	—	6.0	—	—	—
Moulded 60 min./						
150° C. (C stage)	505	1050	6.7	7.8	1.1	0.7
Urea-formald. ¹³						
(cast) (C stage)	310-380	—	3	—	—	—
Aniline-formald. ¹⁴						
(thermoplastic)	250-300	—	7	—	—	—
Polystyrene (mol. weight = 48,000)	383	452	4.1	4.4	1.1	1.0
<i>Glass</i>						
Technical glasses	4,800,000	—	3.5-8.5	—	—	—
<i>Other Materials.</i>						
Cellulose deriva-						
tives ¹⁵ (acetobutyl,						
aethyl, xanthogen)	350-2200	650-4200	± 20	10-12	$\pm 10-20$	—
Carbon steel (0.02 per cent. C.) ¹⁶	20,000	—	29	—	0.05	—
Steel, heat treated (0.025 per cent. C.) ¹⁶	20,000	—	73	—	0.25	—
Steel (best spring) ¹⁶	20,000	—	197	—	0.77	—
Duralumin ¹⁶	8,000	—	36	—	0.17	—

¹¹ Experiments were carried out by means of the bending test, described, for instance, in E. G. Coker and L. N. G. Filon, *Photo-Elasticity*, Cambridge, 1931, p. 183. In this test specially the surface layers are stretched.

¹² E. Evans, *J. Inst. Petr. Techn.*, 1932, 18, 957.

¹³ O. Manfred, *Le Caoutch. et la Gêtahe-Pertak*, 1927, 24, 13,702.

¹⁴ K. Frey, *Helv. Chim. Acta*, 1935, 18, 491.

¹⁵ J. Karger and E. Schmidt, *Z. tech. Physik*, 1923, 6, 124. These values were calculated from observations at room temperature after an ingenious correction for the plastic part of the deformation had been made. E. Valko, *Melland Textilber.*, 1932, 13, 461.

¹⁶ S. Timoschenko and I. M. Lossels, *Festigkeitslehre*, 1928.

over, at this low temperature one may be sure that, in resins for example, there will be no longer any freely rotating particles, so that a comparison with glass at room temperature seems more reasonable.

In the first place, the low values of E and F for asphalts, and the non-hardening resin (colophony) demonstrate the weakness of the secondary bonds in these materials. In the second place, the values for hardening resins at room temperature are interesting. In the case of the phenol-formaldehyde resin, for example, the increase of E by polymerisation from 290 to 595 and of F from 10^{-2} to 6.7 kg. mm^{-2} corresponds to the replacement of secondary bonds by primary bonds as was assumed in § 2. The fact that after a heating process lasting 60 min. at 150°C . no further increase in E takes place, leads to the conclusion that the process of polymerisation has come to an end within that time.

Cooling in liquid air causes E , in the case of the phenol-formaldehyde resin, to increase to 1050 kg. mm^{-2} and F to 7.8 kg. mm^{-2} . This may perhaps be explained by assuming that at room temperature the deformation was still somewhat plastic, although, on the other hand, Hooke's law was found to be applicable up to rupture. We are therefore inclined to consider the deformation of such resins in the C stage as *truly elastic*. Some (calculated) stress-strain curves have been reproduced in Fig. 3. The elongation at the proportional limit (here elongation at rupture) is for all C resins at liquid air temperature 0.5 to 0.7 per cent., i.e., of the same magnitude as for the best spring steel.

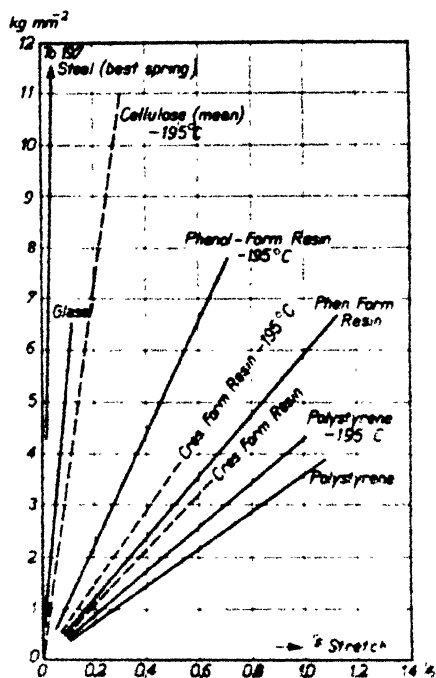


FIG. 3.—Stress-strain curves for hardening Resins in the C stage (in comparison with other materials). The curves for resins have been constructed by starting from the observed deflection figures; compare footnote 11.

§ 4. Explanation of the Low Tensile Properties for Hardening Resins on the Basis of a "Lockerstellentheorie".

Table II. gives a comparison of the tensile strengths of certain materials, as they are observed experimentally, with the tensile strengths which have been calculated on a basis of theoretical considerations. For the resins, the values at liquid air temperature have been tabulated in order to avoid the possibility of plastic deformations.

Many theories¹⁸ have been proposed to explain the discrepancies between observed and calculated values in the case of *crystalline* substances. We shall not discuss all these at length, but mention only the *Lockerstellen* theory of Smekal which seems to be of especial interest in

¹⁸ See next page.

connection with our subject. In this theory structural defects (*Lockerstellen*) are assumed to be present in a crystal. In the neighbourhood of these defects a concentration of stresses is assumed to occur, leading to the observed low "technical strength."

TABLE II.—COMPARISON OF EXPERIMENTAL AND THEORETICAL VALUES OF TENSILE STRENGTH F .

	F (observed).	F (calculated).
Phenol-formaldehyde resin (C stage) at — 195° C.	7.8 kg. mm. ⁻²	4,300 kg. mm. ⁻²
Cresol formaldehyde resin (C stage) at — 195° C.	3.8 ..	3800 ..
Glass normally	3'5-8'5 ..	} 1100 ¹⁷ ..
Glass ¹⁷ under special conditions ..	350-630 ..	
NaCl crystal ^{18, 2} normally	0.6 ..	} 200-400 ..
NaCl crystal under special conditions ..	up to 100 ..	

An explanation of the similar discrepancy between the observed and calculated strength of glass (*cf.* Table II.) may be sought in the theory of Griffith.¹⁷ According to this conception, the discrepancy is partly due to the fact that rupture does not take place simultaneously over the whole cross-section of an amorphous body, but that it starts from accidental cracks (flaws) at which a concentration of stresses is again assumed to occur. Some authors draw special attention to cracks on the surface, while others (*cf.* Joffé, *loc. cit.*¹⁸, page 78) assume the faults to be distributed throughout the bulk of the glass, and to become especially liable to cause rupture when they reach the surface. In our opinion there are several reasons for accepting a similar picture in the case of C resins. The flaws in this latter case will not, however, be accidental and due to some exterior influence (as is assumed by some authors), but will be structural features of statistical nature. They may, therefore, be compared with the *Lockerstellen* of Smekal and we shall consider them as such.

One of the reasons for the existence of these flaws may lie in the fact that not all the CH₂ bridges which are possible on the basis of Fig. 2 will be formed. This becomes comprehensible if we consider Fig. 4 and remember that the benzene nuclei are irregularly arranged and do not lie all in one plane (as should be evident from the figure). At the spot designated by *L* one might assume for instance that the benzene nuclei 5 and 6 are in such relative positions that a chemical reaction between the CH₂OH and the H groups is impossible. This might be due to the fact that the CH₂OH group lies above the plane of the drawing and the H group below it. Further, the presence of occluded reaction products (H₂O) in such a resin might give rise to "holes" in the macro-molecule.

¹⁷ A. A. Griffith, *Phil. Trans.*, 1921, 221A, 163; *Proc. Int. Congress Appl. Mech. Delft*, 1924, p. 55.

¹⁸ Compare A. Joffé, E. Orowan and A. Smekal in: *Proc. Internat. Conference on Physics*, Part II., London, 1934; A. Smekal in: *Handb. der Physik*, 24^{II}, Berlin, 1933. A recent summary by W. G. Burgers and J. M. Burgers is found in the First Report on Viscosity and Plasticity, Roy. Academy of Sciences, Amsterdam, 1935.

¹⁹ This value was extrapolated from experimental figures. Calculations, based on atomic considerations, would lead to much higher values.

for the cresol-formaldehyde resin of > 20 kg. mm.⁻² Even these values are greater than those found experimentally. In order to explain this we should be inclined to assume that a similar consideration is valid for the van der Waals force as that which is given for the primary bonds with reference to Fig. 5. We should thus be inclined to assume also that *as a consequence of the presence of Lockerstellen the maximum combining energy which might be obtained by means of van der Waals' bonds is not reached.*

It is evident that a concentration of stresses at the faults is assumed during deformation in a similar way as is postulated in the theories of Griffith and Smekal and other theories about the subject. The fact that the *Lockerstellen* in the amorphous materials described are less regularly arranged (see Fig. 5b) than is often assumed to be the case in crystals may perhaps be partly responsible for the observation that resin macromolecules (and glass) are brittle and show no glide planes such as are observed with some metals.

Attention must be drawn to the fact that $\frac{F \text{ observed}}{F \text{ calculated}}$ for glass is > 200 , for a resin macro-molecule it is 550 to 1000, and for a sodium chloride crystal 500.

Certain calculated and observed values of Young's modulus may be compared at this point. The following values for the phenol-formaldehyde resin are taken from the paper of de Boer :

E calculated for primary bonds 11,000 kg. mm.⁻²

E calculated for van der Waals' forces > 45 kg. mm.⁻².

The experimental value of about 500 kg. mm.⁻² (in liquid air 1050 kg. mm.⁻²) may point to the fact that the coherence in a resin molecule is effected for a part by van der Waals' forces. The discrepancy between the observed and calculated values of tensile strength is much greater, and it may be ascribed to the fact that the strength is practically determined only by the concentration of stresses at the most "dangerous" *Lockerstellen*, whereas the modulus of elasticity is given through the co-operation of the moduli of several bonds in the molecule.

The explanation of the nature of the above-discussed faults in glass, may be in part similar to that in the case of C resins. It may take into account the formation of net fragments at T_g which are assumed to grow into each other gradually during cooling. In this connection, attention may be drawn to a paper by Lillie²⁰ who (after making many reservations) calculates an increase in aggregate weight from 15,000 to 112,000 when the temperature of glass falls from 1100° C. to 500° C. Such a process of growing into each other of colloidal net fragments would offer an explanation of the fact that (because of unfavourable steric conditions) neither all the ionic bonds nor all the van der Waals' bonds can reach their maximum binding energy. It would go beyond the scope of this paper to attempt to explain all the experimental results of investigations, such as those of Griffith and Joffé, connected with this subject. We hope to have an opportunity to try this at another time.

²⁰ H. R. Lillie, *J. Amer. Cer. Soc.*, 1933, 16, 619. A growing together of large particles has also been observed in the formation of crystals from certain materials, cf. W. von Behren and J. Traube, *Z. physik. Chem.*, 1930, 176A, 1. The attention of the author was drawn to these observations by Prof. Traube during the meeting.

Summary.

1. A general description is given of tensile properties and modulus of elasticity on a basis of cohesive forces of matter.

2. The most prominent theories as to the internal structure of asphalts, resins and glass are discussed briefly.

3. The elastic properties in question have been studied for hardening resins in particular. The modulus of elasticity and the tensile strength of a phenol-formaldehyde resin, for example, are found to be 1050 kg. mm.⁻² and 7.8 kg. mm.⁻², respectively, at a temperature of -195° C. The results have been compared with similar observations for the other materials to be found in the literature.

4. A *Lockerstellen* theory is introduced in the case of resin macromolecules in order to explain the fact that the tensile strength of a phenol-formaldehyde resin, for example, is about $\frac{1}{10}$ of its theoretical value (calculated for the primary bonds). Structural causes for the presence of such *Lockerstellen* are indicated and discussed.

5. The fact that for Young's modulus $\frac{1}{10}$ of its theoretical value is found, may be considered as an indication that, in addition to primary bonds, secondary bonds also play a rôle in resin macromolecules.

Our sincere thanks are due to Dr. J. H. de Boer of the Philips' Laboratories, for his critical assistance, and to Mrs. H. E. Teves-Acly for the translation of the manuscript.

HIGH ELASTICITY OF THREE-DimensionALLY POLYMERISED AMORPHOUS MATERIALS IN RELATION TO THEIR INTERNAL STRUCTURE.

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Introduction.

In this paper the high elasticity of *asphalts, resins and glass* will be dealt with. An attempt will be made to explain the phenomena observed on a basis of the theories about the internal structure of these materials, as these were dealt with in the foregoing paper.

§ 1. High Elasticity of Matter ; Relaxation.

In addition to the true elasticity of rigid bodies attention must be drawn to the *high elasticity* (*ausgiebige Elasticität*) of certain soft materials. It is difficult to give a precise definition of high elasticity since no logical point of departure has yet been discovered. We shall therefore confine ourselves to the following practical description:

An elastic deformation will be called highly elastic when it exceeds a value of about 1 per cent. This limit is chosen in order to exclude crystalline materials (metals) which are considered not to be highly

elastic and for which no higher values than 1 per cent. are usually observed¹ (*cf.* Table I. of the foregoing paper.).

Highly elastic deformations are often, as can be observed with raw rubber, far from truly elastic.

The well-known fact that the elastic after-effect can often be observed practically, only after a rise in temperature, will be accounted for by the introduction of the term *thermo-recovery*.

The credit falls to Whitby² for having pointed out the fact that many materials, which are hard solids at room temperature, have a so-called "elasticity temperature" at which they become rubbery elastic. In connection with the above definitions this temperature will be denoted in the future as the *high elasticity temperature*.

The treatment of all (partly amorphous) materials which show high elasticity would go beyond the scope of this paper. For materials such as wool,³ rubber and muscles,⁴ where the high elasticity seems to be a property of the polymerised chain molecules themselves, reference is made to other sources. The same holds for materials in which the molecules are long in shape and perhaps rigid.^{5, 6} Since it is frequently thought that high elasticity is only encountered in materials having long molecules or micelles⁶—there are even theories which seek to explain high elasticity itself upon this principle⁷—it seems extremely important to show that high elasticity may also be observed to a considerable extent in the case of materials which are polymerised in three dimensions and which therefore probably have globular micelles. It is the purpose of this paper to deal especially with this group of amorphous materials. It will appear that high elasticity and also thermo-recovery are much more frequent properties of matter than is usually assumed in the literature.

In the case of asphalts there are no reasons to deny the presence of globular micelles. Among the resins, as was already mentioned, there are representatives (e.g., polystyrene, polyvinyl-acetate) for which the micelles are generally accepted to be long in shape on the basis of the work of Carothers⁸ and Staudinger.⁹ For other resins, however, such as the natural resins, phenol and cresol-formaldehyde resins and "glyptals," the globular micelle form seems very probable on the basis of investigations by the author.¹⁰ The fact that Newtonian flow may be observed¹¹

¹ From a theoretical point of view this definition is incorrect, for, as Zwicky (*Physik. Z.*, 1923, **24**, 131), showed, one can calculate for NaCl an elastic extensibility of 14 per cent. As such extensions are not actually observed however, our definition seems to be practical.

² G. S. Whitby, *Trans. Inst. Rubb. Ind.*, 1929, **5**, 184; 1930, **6**, 40. In this paper the high elasticity of rubber and some resins with chain molecules is dealt with.

³ Compare for a summary W. T. Astbury, *Fundamentals of Fibre Structure*, Oxford, 1933.

⁴ K. H. Meyer and H. Mack, *Der Aufbau der hochpol. Organ. Naturstoffe*, Leipzig, 1930. E. Mark, *J. Am. Chem. Soc.*, 1934, **56**, 2757. T. R. Griffith, *Canad. J. Research*, 1934, **10**, 786.

⁵ W. F. Busse, *J. Physic. Chem.*, 1932, **36**, 2862.

⁶ This opinion is encountered for instance in the recently issued book of one of the specialists on high polymers: J. R. Katz, *Die Röntgenspektrographie als Untersuchungsmethode*, Berlin, 1934, p. 239.

⁷ K. H. Meyer, G. von Susich and E. Valko, *Koll. Z.*, 1932, **59**, 208.

⁸ W. H. Carothers, *Chem. Review*, 1931, **8**, 353.

⁹ H. Staudinger, *Die hochmol. Verb.*, Berlin, 1932.

¹⁰ R. Houwink, *Physik. Eig. und Feinbau von Natur- und Kunstharzen*, Leipzig, 1934. Compare for glyptal resins: R. Houwink and K. H. Klaassens, *Koll. Z.*, 1935, **70**, 329.

¹¹ G. S. Parks and M. E. Spaght, *Physics*, 1935, **6**, 69.

for certain kinds of glass in a molten condition is an indication that globular micelles are also present in that case. It must, however, be mentioned that some authors suggest the possibility of relatively short, linear molecules.¹²

From considerations as to the oscillations of the atoms one can derive the following relation¹³ for monomeric substances:

$$e = 3KT \text{ per atom } (3KT = 5.96T \text{ cal. per gram atom}), \quad (1)$$

where e is the mean interatomic energy as a consequence of heat motion, K the Boltzmann constant, and T the absolute temperature. At the melting-point T_m of such a system, therefore,^{13a}

$$e_m = 3KT_m.$$

As a first approximation one may say that at a given temperature T , lower than T_m , the energy content of the bond is equal to

$$e_s - e = 3K(T_m - T).$$

Since a rise in temperature causes an oscillation of the atom whose alternating impulses may exceed the mean value $3KT$, local migrations may already have taken place before T has reached the value of $e_s/3K$.

The following consequences of heat motion are important with regard to our present problems. If a body is stretched to a length $l - dl$ the atoms undergo a certain mutual displacement which is connected with a potential (elastic) energy denoted by e_p . If the system is maintained at this elongation there are two possibilities:

(a) If there are atoms for which e_p is larger than $e_s - 3KT$ these atoms can migrate and a partial plastic deformation on release of stress may then be observed. Energy is dissipated as heat.

(b) The atoms for which e_p is smaller than $e_s - 3KT$ will absorb the energy e_p as elastic energy, and this will give rise to internal forces which balance the external ones.

As frequently, however, as an accidental extra impulse caused by heat motion is larger than $e_s - 3KT - e_p$ the atom will migrate. The stored-up potential energy will then be partly transformed into heat. A continually decreasing tension will be necessary to keep the material in its deformed state. This phenomenon is known as *relaxation of stress*, and is expressed by the Maxwell formula

$$F = F_0 e^{-\frac{t}{\lambda}} \quad (3)$$

in which F is the internal tension at the moment t , F_0 is the original tension, and λ a constant, the relaxation time. The value of λ is connected with the energy content $e_s - 3kT$ of the interatomic bonds. It follows from the above considerations that *the maximum amount of elastic energy e_p to be stored up in a body at a given temperature T may be assumed to be a function of the value of $e_s - 3kT$* . This conclusion will be utilised later. The stored-up energy will, however, gradually be transformed into heat.

The fact that in amorphous bodies potential troughs of varying depths

¹² G. Hagg, *J. Chem. Physics*, 1935, 3, 42.

¹³ A. Eucken, *Lehrbuch der Chem. Physik*, Leipzig, 1932, p. 137.

^{13a} Strictly T_m indicates the temperature just below the melting-point, so that the heat of melting is left out of consideration.

e_r may be assumed for various atoms¹⁴ complicates this simple conception to a considerable degree.

§ 2. Observations on High Elasticity and Thermo-elasticity of Asphalts, Resins and Glass.

As has already been mentioned, some authors always connect the possibility of high elasticity phenomena with the presence of long chain molecules. It will now be shown that such phenomena can also be observed with materials for which in section 1 the probability of a globular micelle form has been discussed.

(1) Asphalt.

Experiments by Saal¹⁵ have shown that the high elasticity of asphalt is more pronounced the more the bitumen deviates from a Newtonian

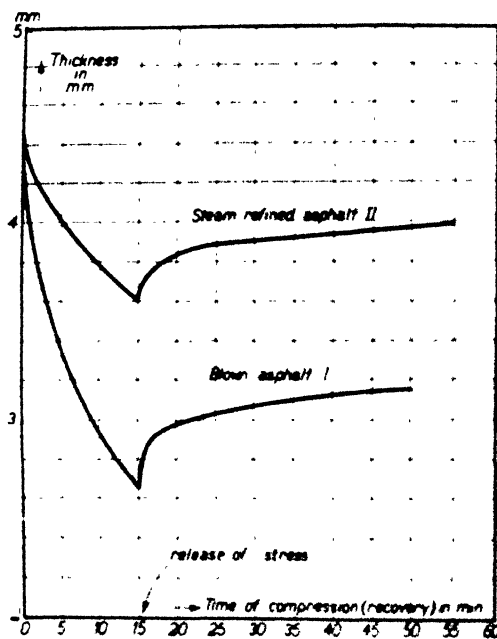


FIG. 1—High elasticity of blown and of steam-refined asphalt (data of F. J. Nellensteyn).

liquid. The data reproduced in Fig. 1 for the high elasticity of certain kinds of bitumen were collected by Nellensteyn¹⁶ by means of a Hoekstra balance plastometer¹⁷. In this instrument a specimen of the material is compressed for a given time. The compressive force is then released and the recovery can be accurately measured. Fig. 1 shows the curves obtained at 30° C. with a blown and with a steam refined asphalt respectively, particulars of which are tabulated in Table I.

Thus an elastic recovery of about 10 per cent. can be observed. It must be noted that this value was higher for the blown asphalt than for the steam refined, although the former was softer.

We shall return to this point in section 4. Another important point is that at 30° C. the viscosity η must be very high. From the well-known fact that at the

¹⁴ See in this connection: H. Mark, *Physik und Chemie der Cellulose*, Berlin, 1932, p. 6.

¹⁵ R. N. J. Saal, *World Petrol. Congress, London, 1933*. Preprint 96. See for earlier investigations, F. T. Trouton and E. S. Andrews, *Phil. Mag.*, London, Edinburgh and Dublin, 1904, 7, 347. The recovery data mentioned here are not made use of because the temperature of test has not been indicated.

¹⁶ We are very much indebted to Dr. F. J. Nellensteyn for these curves, which form part of unpublished work of the Dutch Government Road-Testing Laboratory at The Hague.

¹⁷ J. Hoekstra, *Physics*, 1933, 4, 285.

"ring and ball temperature" η is 1.2×10^4 poises it may be roughly extrapolated that at 30°C . η is at least of the order of 10^{11} to 10^{13} poises, a value which will be encountered with other materials at their high elasticity temperature.

TABLE I.—HIGH ELASTICITY OF ASPHALT BITUMENS AT 30°C . AFTER A COMPRESSION PERIOD OF 15 MIN.

	Compression in Per Cent. of Original Height.	Recovery in Per Cent. of Original Height.
Blown asphalt I. (Pen. at 25°C . = 14; Ring and ball temp. = 111°C .; Asphaltene content = 20 per cent.)	47 per cent.	10 per cent.
Steam-refined asphalt II. (Pen. at 25°C . = 8.7; Ring and ball temp. = 100°C .; Asphaltene content = 34 per cent.)	28 per cent.	7 per cent.

(2) Resins.

It is a well-known fact that the heating (causing polymerisation) of resins of the phenol-formaldehyde type produces a highly elastic, "rubberlike" state, the so-called *B* state. This phenomenon was investigated by Houwink,¹⁰ who was able to show that high elasticity is observed only when a sufficiently large proportion of large micelles may be assumed to be present. Elastic deformations of about 30 per cent. (calculated with respect to the original dimensions), which are to a large extent thermo-elastic phenomena, are described in the above-mentioned work. On further polymerisation, however, the deformability decreases again, and, as is shown in the foregoing paper, only a small true elasticity of the order of 1 per cent. can be observed in the *C* stage. By means of a more efficient technique it has been possible, however, to observe a much more important high elasticity with *B* resins as follows.

Since in the above-mentioned experiments by the author it was not certain that the most suitable high elasticity temperature had been reached, an attempt was made to carry out experiments at a much higher temperature. With the resins under consideration the reaction velocity increases rapidly with temperature, so that, on heating, the resin will quickly be completely transformed into the *C* stage. The observations must therefore be made very quickly. In order to bring the whole mass of the resin rapidly to the desired temperature, the heating was done by means of a pair of hot milling rolls (rubber mixer). When an *A* resin is thrown on the steam-heated rolls, it melts, and, as the polymerisation reaction progresses during milling the *B* stage and finally the *C* stage are reached. During this process samples were taken, of which one observer determined the elastic behaviour, and a second the temperature by means of wrapping the specimen around a thermometer. The temperature so measured is markedly higher than that of the rolls, because of the frictional heat and the heat of reaction developed in the material. The elastic behaviour was studied by marking off a length of 1 cm. on a specimen, stretching it quickly, and releasing it. The distance between the two marks is then measured after release. It must be noted that this technique is far from perfect,

¹⁰ R. Houwink, *Physikalische Eigenschaften und Feinbau von Natur- und Kunstharzen*, Leipzig, 1934. See, for an abstract on thermo-recovery, R. Houwink, *British Plastics Yearbook*, 1935, p. 51.

since the deformation must be carried out very rapidly to exclude the effects of the cooling of the sample on the one hand, and of the progressing polymerisation on the other hand. The data obtained are therefore only approximate values. The alcoholic extract (cold extraction) of the specimens investigated in this way was determined in order to get some insight into the degree of polymerisation.

TABLE II.—HIGH ELASTICITY OF SOME HARDENING RESINS.

Resin.	Time on Mixing Rolls.	Temperature of Specimen.	Deformation in Per Cent. of Original Length.	Recovery in Per Cent. of Original Length.	Alcohol Extract in Per Cent.	Viscosity in Poles* at 60° C.
Cresol-formald. I. (40-45 per cent. meta-cresol.)	11.5 mins.	—	plastic	plastic	75	2.5×10^1
	15.5 "	—	170	100	66	1.5×10^2
	16.7 "	105°	240	130	65	quasi flow
	18.3 "	—	240	170	60	—
	20.5 "	—	240	200	57	—
	21.5 "	—	170	150	55	—
	23.5 "	106°	100	100	44	—
Cresol-formald. II (58-60 per cent. meta-cresol.)	4.1 "	100°	plastic	plastic	68	1.0×10^2
	4.5 "	107°	240	65	54	3.5×10^2
	5.4 "	126°	240	200	47	quasi flow
	5.8 "	124°	240	240	34	—
	6.2 "	120°	170	170	33	—
	6.8 "	—	100	100	30	—
	7.2 "	—	rigid breaks	—	23	—
Phenol-formald.	2.5 "	121°	plastic	plastic	51	—
	2.7 "	124	200	150	45.5	—
	3.0 "	117	rigid breaks	—	37	—
	3.3 "	—	—	—	29.5	—

* 1 poise = 1 dyne cm.⁻¹ sec.

The results of some experiments carried out on two cresol-formaldehyde resins (raw materials containing 40 to 45 per cent. meta-cresol and 58 to 60 per cent. meta-cresol, respectively), and on a phenol-formaldehyde resin (Resol type) have been summarised in Table II.

It is evident from these figures that a temperature of 100 to 125° C. is a suitable high elasticity temperature for these resins in the *B* stage. The highly elastic state could be maintained on the rolls during 8 minutes for the slower cresol resin I, but only during 2.3 minutes for the much quicker cresol resin II, and only during about half a minute for the extremely quick phenol resin. It is further evident that with the cresol resins I. and II. highly elastic deformations of about 200 and 240 per cent. respectively could be observed. The fact that these values were much higher than that for the phenol resin must be ascribed to the extremely quick reactivity of the latter, which makes the taking of samples at the right moment very difficult.

In Fig. 2 some observed data for the elastic recovery are represented, together with data for the change in the alcoholic extract during the steadily increasing polymerisation. It may be taken from Fig. 2 that high elasticity occurs only when a still quite considerable proportion of the resin is soluble. Roughly, a solubility of between 25 and 65 per cent. seems to be necessary for high elasticity of over 100 per cent.

Attention must be drawn to the decrease in the alcoholic extract during the process of polymerisation. This decrease is relatively small compared with the enormous changes in the elastic behaviour. At the utmost (cresol resin II.) a change of 40 per cent. in the alcoholic extract may be taken to correspond to a cycle of increasing high elasticity from zero to 240 per cent. and decreasing it from that value to zero again. This may perhaps be an indication that a very important change in internal structure during this stage of the condensation process is the growing into each other of the net elements. This supposition is supported by observations of the changes in viscosity of the resins. The viscosity η was measured at 60° C. by means of a plastometer and was found to be about 10^6 poises when the first signs of high elasticity could be observed. On further polymerisation only quasi-flow (non-Newtonian flow) was observed, which means that η becomes dependent upon the magnitude of the applied shearing stress. This fact has already been connected with the formation of continuous networks in a resin.¹⁹

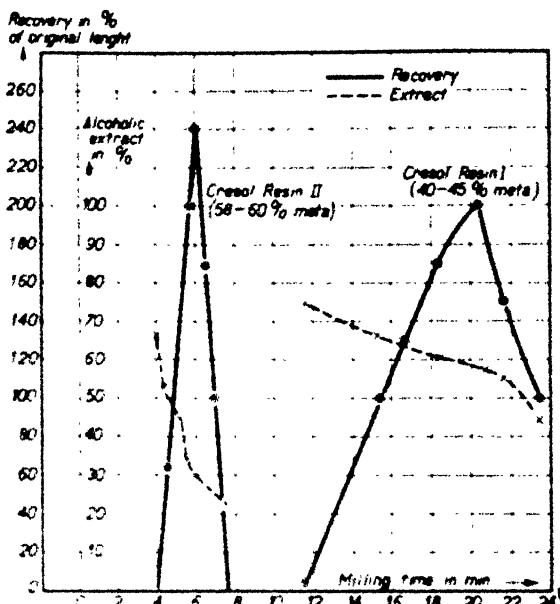


Fig. 2. Relation between high elasticity and alcoholic extract of two cresol-formaldehyde resins during polymerisation at about 100-125° C.

TABLE III. HIGH ELASTICITY OF GLASS.²⁰

Temperature.	Viscosity in Poises.	Deformation Degrees of Twist.	Recovery Degrees of Twist.
575° C.	1.1×10^{12}	30	6
660° C.	2.3×10^{11}	50	19

(3) Glass.

Trouton and Andrews¹⁸ showed that high elasticity phenomena can also be observed in the case of glass. They could study the viscosity of glass

by applying a constant torque to a cylinder of soda glass, and observing the relative motion of the ends. After release of the torque they could

¹⁹ R. Houwink, (*loc. cit.* 18), p. 138.

²⁰ In a previous study by the author (Houwink,¹⁸ p. 134) the work of M. So was cited erroneously in this connection. The recovery data observed by So are too small to justify the term high elasticity. They lie between 0.06 and 0.22 per cent. instead of being 1 per cent. as was calculated by the author. In So's experiments the temperature was too high to obtain a significant high elasticity.

study the recovery. From these experiments the data in Table III. are given.

It must be noted that the two experiments were not carried out under exactly the same conditions. The torque in the first case was 10/6 times that in the second case. No direct comparison can therefore be made. It is important to note, however, that, just as with asphalt, the high elasticity is observed in a viscosity range of 10^{11} to 10^{12} poises, which is in the neighbourhood of the transformation interval, that is to say when the material is in the (assumed) gel state, where freely rotating structural units are assumed to co-exist along with "solid" units.

§ 3. Explanation of High Elasticity.

In order to explain the high elasticity observed in materials with globular micelles an example of deformation worked out mathematically by van Dongen²¹ will be dealt with.

In Fig. 3 the deformation of a compact body P is compared with that of an "open" body Q . The end planes of Q are assumed to be open so

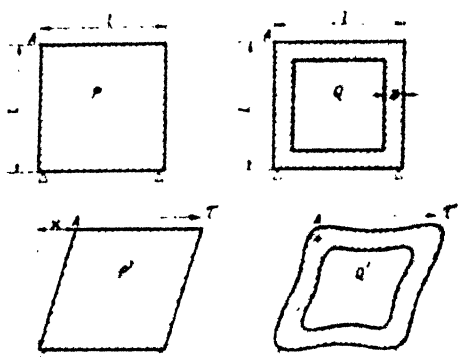


Fig. 3 - Elastic deformation of a compact body P and of an "open" body Q .

that it forms a sort of rectangular "tube". The substance of which the bodies P and Q are constituted is assumed to be incompressible and to possess a modulus of elasticity E and a yield value f . It is further assumed that the contraction ratio m of the material is 4 and that the space inside Q is filled with an incompressible fluid. Under the application of a certain shearing stress τ the body Q will be deformed in quite a different way from P , and if one assumes that

the experimenter does not know that Q is hollow, he will, for example, follow the displacement of point A in his measurements, and draw conclusions from the measured deformation X under the influence of a given τ . In such a case he will then find for Q a quite different modulus of elasticity and a quite different elastic deformation on the attainment of the yield value from that for P . If this "apparent modulus of elasticity" is called E' van Dongen has derived the following relation:

$$\frac{E}{E'} = \left(\frac{l}{a} - 1 \right) \left(\frac{1}{3} \left(\frac{l}{a} - 1 \right)^2 + 1 \right). \quad (4)$$

From this it follows that the apparent modulus of elasticity is, in the first approximation, proportional to a^3 , i.e., to the third power of the thickness of the wall. The following expression may be derived for the "apparent" specific elongation upon attainment of the yield value:

$$\frac{\epsilon'}{\epsilon} = \frac{a}{l} \left(\frac{1}{3} \left(\frac{l}{a} - 1 \right)^2 + 1 \right). \quad (5)$$

²¹ Our sincere thanks are due to Ir. J. R. J. van Dongen of Eindhoven, for his kindness in working out this example on a basis of theoretical mechanics.

in which ϵ is the specific elongation of the material itself and ϵ' is the apparent specific elongation. As a first approximation one may thus say that the apparent specific elongation at the limit of flow is inversely proportional to the thickness a of the wall.

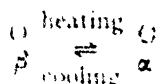
On the basis of Hooke's law it follows that the "apparent yield value is proportional to a^2 .

The equations given above are only approximately valid when the deformations are small with respect to the dimensions and when the thickness of the wall a is small with respect to l . They are still sufficiently accurate when $\frac{a}{l} \leq 0.3$.

From this point of view it becomes understandable that a much lower modulus of elasticity, a higher elastic elongation and a lower yield value are observed for a gel consisting of cells of a solid substance filled with a fluid, than for a material which consists entirely of solid matter. Expressing this in terms of energy one may say that in the case of the body Q a much larger deformation X is possible before a bond between the structural elements will have absorbed an amount of energy equal to $\epsilon_0 = 3KT$, the amount necessary for its distortion, than in the case of the body P . The causes of the high elasticity of three-dimensionally polymerised materials may be more easily understood by analogy with such a model. We shall use this concept in our own treatment of the hardening resins, and then apply the knowledge gained thereby in the cases of asphalts and glass.

(α) A Resin in the A Stage.

Fig. 4a represents a liquid resin in which chiefly freely rotating molecules denoted as α units are assumed to be present. In such a liquid resin there may be an equilibrium between the number of α units present and the number of so-called β molecules, which are molecules attached either to each other or to γ units (see below) by means of secondary bonds. As long as the equilibrium



is definitely in favour of the α units, so that no yield value can be measured, the resin may be called a liquid. It is supposed, that even in such a liquid resin some molecules may be linked to one another by primary forces. Such a combination forms a γ unit.

When a shearing couple $\tau = \tau'$ acts on the liquid A resin it is obvious that it will cause the units to flow, and on release of the stress no elastic phenomena are to be expected.

Upon cooling the liquid resin the situation represented in Fig. 4b will gradually be reached where the number of β units has increased to such a degree that they begin to act as bridges between the γ groups. In this way a kind of network may be formed in which the structural elements cohere for a great part by means of secondary forces. Those parts of the structure where "holes" are present (filled with α units) are comparable with the open structure of Q in Fig. 3. One might therefore expect to observe the phenomenon of high elasticity. The fact that this is not the case to a very considerable extent must in our opinion be ascribed to the following. In the temperature range in which α and β units co-exist, the energy ϵ_0 of the bonds between the β units (about 1 kg. cal.

per gram equivalent \approx heat of fusion of phenol) is only slightly higher than the kinetic energy $3KT$ of the heat motion of these units. Therefore the network cannot store up energy of elastic deformation e_e to a considerable extent within this range. If a quantity of energy e_e is stored up, it will very easily be dissipated by relaxation. Most of the energy added to the system as a whole will be expended in the form of a plastic deformation of the body.

Further cooling of the system will lower the value of $3KT$, and therefore increase the energy difference $e_e - 3KT$, thereby favouring the possibility of the storing up of energy and the consequent high elasticity. At

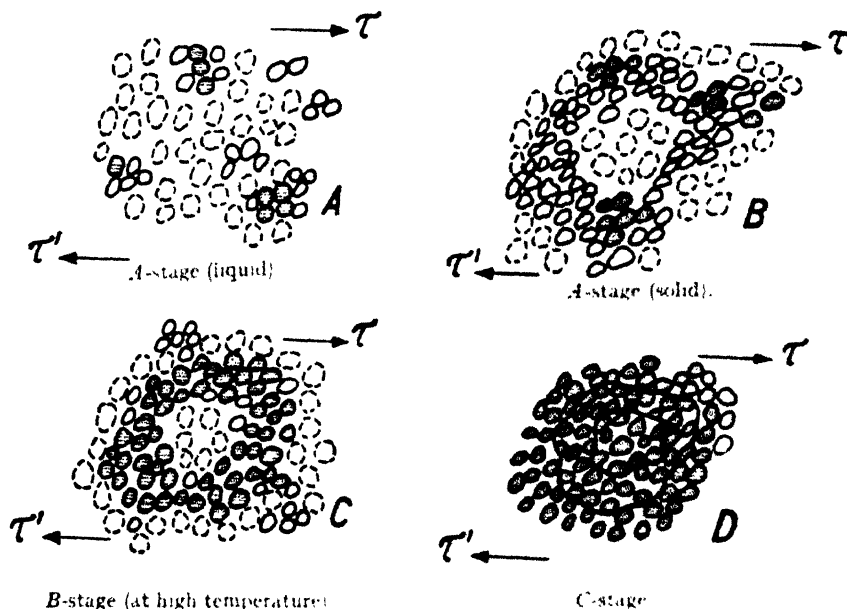


FIG. 4.—Scheme for the explanation of the elasticity phenomena of a three-dimensionally polymerising resin.

$\tau \sim \tau'$. Shearing couple

$\bigcirc \bigcirc \bigcirc$ α units, freely rotating molecules (soluble)

∞ β units, fixed by means of secondary bonds (soluble)

--- γ units, fixed by means of primary bonds (insoluble)

Such a conglomerate of γ units will be denoted as a micelle. The α and β units together will be soluble in solvents in which the A resin itself is soluble

the same time, however, the number of β units increases at the expense of the α units, so that a condition more and more like that of P in Fig. 3 will be reached. This behaviour will counteract the positive factors for high elasticity according to van Dongen's formulas. The fact that some high elasticity has been observed with asphalts indicates that when $\eta = 10^{11}$ to 10^{13} poises the conditions are especially favourable. We shall return later to this subject of the high elasticity of asphalt and glass.

Let us now consider a hardening resin in the B stage. Reference to Table II. recalls the fact that, when the degree of polymerisation necessary for high elasticity has been reached, the resins are only partly soluble,

and Newtonian flow is no longer possible (at 60° C.). As has already been mentioned, these facts, and the relatively small decrease of the alcoholic extract compared to the large increase in elastic behaviour which is observed during the condensation process on the rolls, may be indications that at this stage large micelles are growing into each other to form a three-dimensional network throughout the mass. In Fig. 4c an element of such a network is represented. This net is principally different from that of Fig. 4b because of the fact that *most of the elements are held in their relative positions by primary bonds*. At room temperature β units are still present in the system. If such a *B* resin is heated until most of the secondary bonds between the β units are broken (the situation in Fig. 4c) *a network of γ units still remains which is capable of storing up a large amount of potential energy in its elements*.

The resin under consideration now shows a great resemblance to *Q* of Fig. 3, and if we accept this structure for a *B* resin, its high elasticity may be explained on the basis of formula (4) and (5). The fact that the elastic recovery is a *thermo-recovery* may be ascribed to the high viscosity of the α and β units at room temperature, which prevents the deformed network from recovering its original shape.

Table II. shows that the content of α and β units together is still about 25 to 65 per cent. In a resin of the phenol-formaldehyde type (and also of the glyptal type) the viscosity at 20° C. of the $\alpha + \beta$ units present will be at least about 10⁶ poises.²² This very high value for the viscosity offers an explanation of the lack of recovery of the *B* resin at room temperature.

If the temperature is raised, the conditions for recovery become favourable, since the viscosity coefficient η of the "liquid" decreases by a factor of 10 for each 10 degrees increase in temperature.¹⁰ Roughly speaking, the velocity of recovery therefore also increases by a factor of 10 for every 10 degrees increase in temperature. The value of η for the $\alpha + \beta$ units at 120° C. appears to be about 10 poises,²² so that the $\alpha + \beta$ units at that temperature may be compared with a liquid like glycerol at room temperature.

According to a recent investigation of Derksen²³ a maximum of 50 per cent. of water can be taken up in the crystallites of gelatine, while up to 950 per cent. can be stored up around and between the crystallites. The high elasticity of such a gel as gelatine, not being thermo-elasticity, may probably be explained by the lower viscosity of the large amount of liquid (water in the case of gelatine) compared with the viscosity of the liquid in an isogel like a resin at room temperature.

Upon cooling a highly elastic *B* resin the α units will be gradually transformed into β units again, and the situation *P* of Fig. 3 is more and more nearly reached, where high elasticity is no longer possible. The more such a body is cooled, the more truly elastic become the deformations due to the decrease in heat motion, and therefore in capacity to migrate, of the β molecules present.

The situation in the case of *resins in the C stage* may be represented

²² This value can be found by extrapolation for a phenolformaldehyde resin of Novolak type (see Houwink, *loc. cit.*¹⁰, Fig. 30).

²³ J. C. Derksen, *Diss. Utrecht*, 1935.

by Fig. 4d, where only γ units are present which form (when the *Lockerstellen* are neglected) one large macromolecule. A "net element" has been drawn in this figure of the same shape as in Fig. 4c, but here surrounded only by γ units. The analogy with P in Fig. 3 is here obvious, and the impossibility of high elasticity is due to the same considerations.

An explanation of the high elasticity of *glass* may be sought on the basis of the foregoing discussion. In Table III, it will be seen that the high elasticity is especially observed at a viscosity corresponding to the transformation interval. During this interval γ units may be supposed to be present along with α units (perhaps also β units), so that a structure of the type represented in Fig. 4c may be assumed. The question then arises as to whether or not high elasticity as in a B resin (200 to 240 per cent.) will be encountered, and may be answered by examining whether or not the necessary conditions for the storing up of elastic energy e_p , mentioned in section 1, are satisfied.

Keeping in mind the fact that high elasticity in glass was observed within a viscosity range of about 10^{11} to 10^{13} poises, that is to say, in the neighbourhood of the transformation interval (see § 2), one may immediately conclude that *no great quantity of energy can be stored up in the glass at that high temperature*. It must further be remembered that for a B -resin high elasticity was observed to be connected with the occurrence of quasi flow. For the resin this may indicate that strong net fragments have been formed with a high energy content compared with the value of $3KT$, and that these fragments can still be deformed under the influence of shearing stresses because they are partly separated to some extent by α units. In the case of glass this viscosity indicates that the softening point is approaching, so that groups of molecules are formed which cohere with an energy content of about $3KT$.

The reason for this difference between a B resin and glass lies in the fact that, in the case of the resin, a *chemical reaction* is necessary to cause the formation of γ units from α units, and it *results in a jump in energy content*, of the γ units compared with the α units. In the case of glass, however, the transition $\alpha \rightarrow \gamma$ is a more gradual process *without sudden change in energy*, and is much more nearly analogous to the gradual transition $\alpha \rightarrow \beta$ in a non-hardening resin. This conception is supported by the work of Berger cited in the foregoing paper, where it is demonstrated in full that during the transformation interval there is no sudden change in volume, heat content or other quantities of state.

In the case of *asphalt* the observation of high elasticity at a viscosity of about 10^{11} to 10^{13} poises is an indication that, under these conditions, a network of the type of Fig. 4b is present which is able to store up a certain amount of potential energy. This network will contain about 20 to 30 per cent. of γ units (asphaltene micelles), and further probably chiefly β units. The observation that high elasticity is more pronounced with blown asphalts may perhaps be connected with their higher asphaltene content, which would result in a closer contact²⁴ of the asphaltene micelles. This supposition is confirmed by the fact that such blown bitumens exhibit no Newtonian flow. High elasticity phenomena of some hundred per cent., as are encountered in hardening resins, might be expected in the case of asphalts only if interlinks of high energy

²⁴ Compare F. J. Nellensteyn, *World Petroleum Congress*, 1933. Preprint 56.

content could be created between the asphaltene micelles, and if the petrolene content could be lowered below about 70 per cent.

It must be admitted that many points of the above discussion are still rather vague because of the lack of accurate experimental data and theoretical insight. Our only intention has been to make a preliminary attempt to show the accordance between the outstanding theory and the observations of elasticity. Very much more experimental work is necessary before the problems of this subject can be entirely solved.

Summary.

1. A general description is given of the phenomena of high elasticity of matter. The relation is shown between the maximum amount of elastic energy which can be stored up in a material and the energy content of the bonds.

2. The results of certain experiments on high elastic behaviour of the above-mentioned materials are dealt with. The hardening resins are further studied in particular. A high elasticity of up to 240 per cent. can be observed for hardening resins at a high elasticity temperature of about 120°C., and the relation is shown between the conditions for this behaviour and the formation of insoluble, elastic, three-dimensional networks.

3. High elasticity can also be observed with materials like asphalts and glass but not to the same extent as with *B* resins. In the case of asphalts and glass it is only of the order of 10 to 20 per cent. For the materials described the possibility of high elasticity seems to be connected with a viscosity of the order of 10^{11} to 10^{12} poises (near the transformation interval).

4. Calculations are given to explain the changes of Young's modulus, yield value and strain at the yield value, when compact bodies are transformed into open net structures.

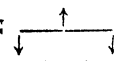
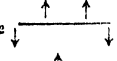

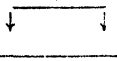
5. An attempt is made to give a rough explanation of the high elastic behaviour of asphalts, resins and glass on the basis of the energy content of their internal bonds with reference to the internal net theory developed.

Our sincere thanks are due to Dr. J. H. de Boer and J. R. J. van Dongen, of our Philips' Laboratories, for their critical assistance, and to Mrs. H. E. Teves-Aelv for the translation of the manuscript.

GENERAL DISCUSSION.

Professor H. Mark (*Wien*) said: In connection with the interesting contribution of Dr. Houwink I want to refer also to the paper of Dr. de Boer. It seems to me very reasonable to try now to get quantitative results in the theoretical interpretation of the mechanical behaviour of synthetical resins. Our spatial models of the structure of these substances and our general knowledge of the intermolecular forces are already so well founded that it seems permissible to undertake such a task.

If one seeks to calculate quantitatively the modulus of elasticity of high polymeric substances which are built up from long carbon chains, I think one must take into account not only those effects which Dr. Houwink has discussed, but also the fact that the directions of the chemical main valence bonds are not rigid, but can be bent from their original direction, if one applies sufficient energy. From the theory of internal tension of ring molecules and from spectroscopic data one can estimate the amount of these energies. The following values are taken from a book of H. A. Stuart:—

Substance.	Energy to bend the Valence out of its Original Direction.		Distance of the Atoms.
	5°.	10°.	
HCN 	~ 200 Cal./Mol.	~ 800 Cal./Mol.	H — C = 1.08 Å.
C ₂ H ₂ 	~ 200 Cal./Mol.	~ 800 Cal./Mol.	H — C = 1.08 Å.
CO ₂ 	~ 450 Cal./Mol.	~ 1750 Cal./Mol.	C — O = 1.15 Å.
CS ₂ 	~ 300 Cal./Mol.	~ 1200 Cal./Mol.	C — S = 1.5 Å.

If one compares this with the energy, which is necessary to stress a chemical main valence bond in its own direction it is seen that the latter energy is much larger than the former.²⁵ Therefore one has to assume that at the start of the elastic stress the valences are first bent from their original direction and then are stressed themselves.

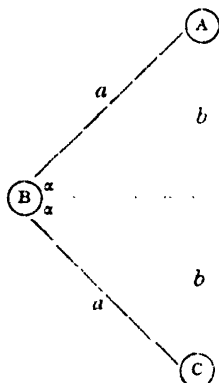


FIG. 1.

If we want to increase the distance between A and C (Fig. 1) by 10 per cent. we have the two possibilities: we can increase the angle α by $d\alpha$ and keep a constant or we can increase a by da and keep α constant.

The distance between A and C is always given by

$$2b = 2a \sin \alpha.$$

The two possibilities of increasing it are

$$db = a \cos \alpha d\alpha$$

and

$$db = da \sin \alpha.$$

If we want to get the same relative increase, namely, 10 per cent we have to write

$$\frac{db}{b} = 0.1 = \frac{a \cos \alpha d\alpha}{a \sin \alpha} = \cotg \alpha d\alpha,$$

$$\frac{db}{b} = 0.1 = \frac{da \cdot \sin \alpha}{a \cdot \sin \alpha} = \frac{da}{a}.$$

Taking for α and a the values, which hold for a carbon chain, we find

$$d\alpha \sim 8^\circ$$

and

$$da \sim 0.15 \text{ Å.}$$

In the first case we want between 1000 and 1500 cal./mol., in the second certainly more than 5 or 6000 to produce the same elongation db .

I tried some time ago to calculate the modulus of elasticity of the diamond from the well-known lattice of this substance or the assumption, that the valence directions are initially modified, and Professor Meyer has recently accomplished similar considerations. One gets the right order of magnitude, but cannot compare this result with the experiment

²⁵ To stress the C—H bond to the extent of 0.1×10^{-8} cm. one requires about 5000 cal./mol. and to stress the C=O bond in CO₂ for the same amount one needs more than 11,000 cal./mol.

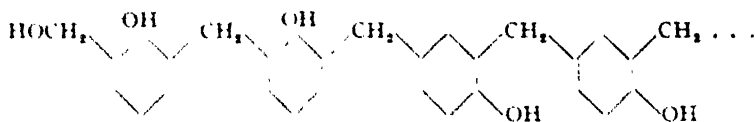
because the modulus of the diamond is not measured in certain crystallographic directions.

I would like to add, that in the case of rubber-like elasticity a statistical effect has to be taken in account. This was first derived by Professor Meyer from the temperature-dependence of the elastic behaviour of rubber and was recently discussed in detail by Guth and myself. It is an effect which leads to very interesting results as to the behaviour of long chain molecules. To what extent it plays a rôle together with the other effects quoted by Dr. Houwink must be tested in every special case by careful measurements of the influence of temperature on the extension curve.

Finally very interesting considerations on the elasticity and plasticity of high polymeric substances were made by Dr. O. Kratky and discussed at the meeting of the Bunsengesellschaft in Berlin last spring. The results seem to be in good agreement with what Dr. Houwink has said.

Professor E. K. Rideal (*Cambridge*) said: Calculations of the tensile strength of a material involve the assumption of instantaneous or simultaneous withdrawal of two planes of atoms from one another and that each atom is linked to its opposite partner by one of two types of linkage, the covalent or the dispersive Van der Waals' type. It has been frequently pointed out that withdrawal of a covalent linked chain of atoms from the interior of the surface may take place instead of the breakage of a covalent link at the surface, if the former operation takes place more readily. It must also be observed that the material in a polymer is not fibrous as in cotton and in consequence of the flexibility of bent chains the mechanism of rupture may not be instantaneous or simultaneous over the total area of the specimen but one part of the extending and separating interface may stretch more than another.

Professor K. H. Meyer (*Genève*) said: Dr. Houwink has asked whether in my opinion rubber-like extensibility is always connected with the presence of long-chain molecules. The extensibility can have different origins. The elasticity of a steel spring is not connected with the presence of long molecules, and a similar mechanism might be found in other elastic materials. But in all homogeneous substances which show rubber-like elasticity, one could always establish the presence of long molecular chains, and I can very well imagine that chains are also the cause of elasticity in Houwink's substances. In the phenol formaldehyde condensation products the elasticity is observed only at a certain degree of polymerisation. We must assume that, at first, the phenols build up chains with the formaldehyde, e.g.,



It seems possible that the elasticity is due to this state, and that the cross linkages, which are formed in the subsequent phases of the polymerisation process inhibit the extensibility by formation of a solid tridimensional network.

Dr. J. H. de Boer (*Eindhoven*) said: Perhaps there may be added still one argument for the existence of *Lockerstellen* of the type indicated by Figs. 5a and 5b of Dr. Houwink's first paper. The dielectric behaviour of these condensation products supports this argument. This behaviour can be understood if little holes are assumed in which some electrolyte may wander to and from in the electric field. Now, from the paper of Dr. Houwink we see that such holes are very probable and that they may contain water of condensation and free OH-groups.

Professor H. Staudinger (*Freiburg i. Br.*) said: Very many elastic materials have a somewhat complicated structure, e.g., vulcanised rubber, factis and the elastic phenol-formaldehyde condensation products. In

order to get an insight into the relations between elasticity and molecular structure, simple compounds of high molecular weight ought first to be investigated (and particularly the polymeric homologous series of such substances). The investigation of a number of polymeric hydrocarbons (e.g., rubber (polyprenes), hydorrubber (polypranes), polyisobutylenes), has proved that pronounced elastic properties are possessed only by the products of highest molecular weight and are entirely absent in the case of hemicolloidal products. Therefore the high elasticity of these substances must depend on the fact that they are built up of large macromolecules. Since saturated aliphatic hydrocarbons can also be elastic it follows that, contrary to previous suggestions, the double bonds in the rubber molecules are not essential to an explanation of the elasticity. However, with these observations the general question of elasticity is not yet definitely cleared up. Hard tough eupolystyrene becomes elastic when heated to 120°-150° and furthermore also by the addition of small amounts of solvent.²⁶ According to this it is very likely that under suitable conditions all high molecular weight substances, which are built up of thread molecules, assume elastic properties.²⁷

Mr. N. J. L. Megson (*Teddington*) said: Referring to the formation of "Lockerstellen," which are suggested as partly due to structural difficulties in the elimination of water between methylol and hydroxy groups: evidence supporting this idea is contained in the results quoted for the two types of phenolic resins employed. Cresylic acid, on account of its *m*-cresol content should give a resin with structure analogous to that of phenol resins, together with a high proportion of long chain molecules derived from the *p*-cresol content. The intrusion of these long chain derivatives between branches of the *m*-cresol resin may be an additional factor in preventing elimination of water, thereby increasing the tendency to formation of *Lockerstellen*. Experimentally, cresylic acid resins possess a tensile strength of 3.8 kg./mm.² instead of the theoretical value of 32 kg./mm.² which is a lower *proportional* value than that shown by phenol resins (7.8 kg./mm.² experimentally compared with the theoretical value > 39 kg./mm.²).

Dr. L. C. Verman (*Teddington*) said: In the course of the discussion, various points have been raised which indicate that the calculations of modulus of elasticity and tensile strength as presented in the paper may only be regarded as approximate. It is therefore not surprising to find that the calculated values are much higher than the experimental. It appears that probably too much stress has been laid on the existence of *Lockerstellen* and their influence in determining the mechanical properties of resinous materials, etc. It would be interesting, however, to demonstrate the existence of *Lockerstellen* directly in resinous materials and, if possible, to determine the extent of their influence. Methods of fatigue test commonly used in testing metals may prove useful in this connection.

Dr. R. Houwink (*Eindhoven*), said, in reply to Professor H. Mark: Dr. de Boer and I wish to express our sincere thanks for the very fundamental suggestions made. When considering polymers, built up from long carbon chains the bending phenomena pointed out by Professor Mark must, of course, be taken fully into account. In our opinion the situation with amorphous three-dimensional polymers in the C stage is, however, different, in so far that the conditions necessary for displacement of atoms A and C in regard to B will not be very favourable. In the ideal case (on which are based the theoretical calculations) A, B, and C are bound to their neighbours by means of primary bonds and, therefore, the possibility of bending the valences AB and BC out of their original direction will be materially decreased. *This is fundamentally different in the case of materials such as*

²⁶ H. Staudinger and H. Machemer, *Ber.*, 1931, **62**, 2922.

²⁷ Compare H. Staudinger, *Die hochmolekularen org. Verbindungen*, Verlag Springer, 1932, p. 122.

rubber, where the atoms *A*, *B* and *C* are bound to any other carbon atom of a neighbouring chain merely by means of readily deformable secondary bonds.

We nevertheless agree with Professor Mark to the extent that the effect he mentions should not be neglected in the calculation of mechanical properties. The only difficulty is that such a calculation would become extremely difficult. There is one point in our favour, namely, that by taking the bending effect into account, the theoretical values for the tensile strength would become still higher, because the energy necessary for the bending process must be added to the energy of stressing, calculated in de Boer's paper. As de Boer has calculated *minimum values* he has gone along safe lines. With regard to the theoretical value for the modulus of elasticity, this may indeed become lower if the bending effect should play an important rôle. From a scientific point of view it would be very interesting, therefore, if exact calculations, taking the bending effect into account, could be carried out.

It seems to me that the statistical effect (Joule effect as a consequence of changes in internal energy on deformation) in high-elastic substances, mentioned by Professor Mark, will not play an appreciable rôle in the experiments on three-dimensionally polymerised materials, described in my second paper. There are three separate groups of authors, namely (a) Meyer and Ferri,²⁸ (b) Wiegand and Snyder,²⁹ and (c) Hencky³⁰ from whose work one may take it that this Joule effect in rubber is not observed when it is stretched less than roughly 300 per cent. The first and second-named investigators find this limit to be 400 per cent. and 300 per cent. respectively. Hencky on purely theoretical grounds calculates it to be 270 per cent. As the elastic deformations described in my paper do not exceed 240 per cent., it seems therefore improbable that the *Abstoßungsdruck* of K. H. Meyer and co-workers³¹ has to be taken into account in the case of resins, glass and asphalt. This seems to be the more true since the conditions for orientation in 3-dimensional materials seem to be much less favourable than in materials with long chains. Notwithstanding these arguments I agree with Professor Mark that an investigation on this subject would be extremely interesting.

With regard to the supposition of Professor Rideal that a withdrawal of some covalent linked chain from the surface of rupture may occur when such a chain is attached to other atoms by means of van der Waals forces, it may be said that this situation is for the greater part in agreement with the picture which has been postulated in the *Lockerstellen* theory for resins. In my opinion a withdrawal of irregular blocks (instead of chains) in the case of amorphous three-dimensional polymers may actually occur and, for this reason, it seems very probable to me that the mechanism of rupture will involve an uneven distribution of stress over the separating interface. It is also partly for this reason that the actual modulus of elasticity *E* may be expected to be some mean between *E* for the covalent bonds and *E* for the van der Waals bonds. As mentioned in my paper, the experimental value of about 1000 kg. mm.⁻² for *E* in liquid air is a strong argument for this conception, because it lies between the theoretical values of 11,000 kg. mm.⁻² for covalent bonds and > 45 kg. mm.⁻² for van der Waals bonds.

With regard to the remarks of Professor K. H. Meyer related to the steel spring, I would like to say that the high-elasticity of such a spring is based on the same principles as used in Fig. 3 of my second paper. To Professor Meyer and Professor H. Staudinger together I should like to say that in the highly elastic resins described in my second paper the presence of long molecular chains is very improbable in the initial stage of

²⁸ K. H. Meyer et C. Ferri, *Helv. Chim. Act.*, 1935, **18**, 570.

²⁹ W. B. Wiegand and J. W. Snyder, *Trans. Inst. Rubb. Ind.*, 1934, **10**, 234.

³⁰ Hencky, *Trans. Am. Soc. Mech. Eng.*, 1933, **55**, 55-8-45.

³¹ K. H. Meyer, G. von Susich and E. Valko, *Koll. Z.*, 1932, **59**, 208.

condensation as well as at the end stage. This has been pointed out in my book (*Phys. Eigenschaften und Feinbau von Natur- und Kunstharzen*, Leipzig, 1934). The best proof that the high-elasticity is not to be ascribed here to the presence of long chains seems to be that *no high-elasticity is observed with these resins so long as they are soluble*. On the contrary, the high-elasticity is only observed in a stage of condensation in which the resins are to a large extent insoluble.

I fully agree with Mr. N. J. L. Megson that the presence of *p*-cresol (and *o*-cresol) in the crysilyc acid resins will increase the tendency to formation of *Lockerstellen*. I do not believe, however, that the *p*-cresol resins will be present as long chains. If in the relatively short reaction time necessary to reach the B-stage in my experiments, the *p*-cresol formaldehyde molecules should have reached some appreciable magnitude (which in my opinion is very improbable) they might perhaps be present in a coiled-up form, but not as extended chains (see the foregoing answer).

To Mr. L. C. Verman I would like to say that the approximations made by Dr. de Boer in his calculations as to the strength of resins have always been carried out in such a way that he adopted the most unfavourable conditions. His theoretical values are therefore *minimum values*, and from this point of view there is no reason to say that too much attention has been paid to the *Lockerstellen*. Fatigue tests may be very important from a point of view of testing materials but, in my opinion, they do not seem very adequate in procuring insight into structural problems, because such tests are amenable only with great difficulty to mathematical treatment.

INORGANIC SUBSTANCES WITH RUBBER-LIKE PROPERTIES.

By KURT H. MEYER (*Geneva*).

Received 15th July, 1935.

Two inorganic substances with elasticity similar to that of rubber are described in the literature of the subject, *viz.* elastic sulphur and poly-phosphonitrilic chloride. In this paper we shall deal with investigations of both.

It is common knowledge that sulphur heated to 170° becomes highly viscous; if then cooled, *e.g.*, by plunging into water, it yields an amorphous elastic product.

If threads of this amorphous product are stretched, they show a double refraction, and, as Trillat¹ has found, develop a fibre-diagram. With Go the author² has examined this diagram, and deduced from it the following arrangement of the sulphur atoms: long chains of sulphur atoms, linked by strong homoeopolar valences, are arranged parallel to the direction of stretching. Their special position in the elementary cell is shown in Fig. 1.

In a recent publication, B. E. Warren³ has made it clear that common sulphur is made up of 8-atom rings. The molecular weight of the elastic form S_n is not known, but seems to be very high.

We know from earlier work that the melting of sulphur produces an equilibrium between the two forms, and this shifts, at higher temperatures, in favour of the chain-sulphur. About 1000 calories per gram atom S are consumed in the transformation of S_8 into S_n .

¹ 1932 (4), 51, 248.

² *Helv. chim. act.*, 1934, 17, 108.

³ *J. Chem. Physics*, 1935, 3, 6.

Endothermic reactions can only proceed if there is at the same time an increase in entropy—in other words, if the atoms, in the endothermic form, have more room to oscillate, that is to say, have a greater "phase-volume." During the process of transformation, however, there is no increase in volume, but, on the contrary, a slight decrease; this, therefore, can only be explained on the ground that the sulphur atoms in the chain are more mobile than those in the rings. In view of this, the chains must be flexible. This entirely agrees with our conception of the nature of elasticity, which has recently been published.⁴

Some light is thrown upon the kinetics and mechanism of the polymerisation and depolymerisation of sulphur $S_8 \rightleftharpoons S_n$ by the following facts, some of which were already known, while others have been only lately observed by Sievers. Both polymerisation and depolymerisation are catalysed by light; this indicates that S_8 molecules are split up by a quantum and then, in the manner of a chain reaction, unite with other sulphur rings, whereupon the product then produced becomes active, and is capable of splitting up other rings and attaching them to the rapidly-growing chain. Conversely, a completed chain in a metastable state may be expected to disintegrate rapidly as soon as activation takes place at any point.

If purified sulphur is heated in pyrex vessels, it remains a thin fluid up to 172° , or a few degrees higher if in the dark. Above that point, it changes quite suddenly into an orange-coloured, resinous substance, and during that process the temperature falls by about 1° . If now carefully cooled, the resinous substance quickly liquefies again, and, when it is re-heated, the transformation

into the resinous substance takes place at a lower temperature and more gradually. If this process is repeated, the transformation becomes more gradual every time, and all the phenomena of retardation disappear. The metastable fluid state, which is easily obtainable in virgin sulphur at 170° , can no longer be secured. The explanation, we think, is, that in the process of heating, active molecules, on which chains form very rapidly, appear only at relatively high temperatures; in the process of cooling, the chains break away, but leave nuclei which, on re-heating, quickly establish equilibrium (formation of chains).

The polymerisation of metastable virgin sulphur at 170° can also be initiated by the addition of a very small quantity of polymerised product or product in process of polymerisation.

If sulphur is heated to much higher temperatures (about 300°), its viscosity decreases and it turns brown. If it is then cooled, the viscosity rises again, but not up to the maximum that is reached at a

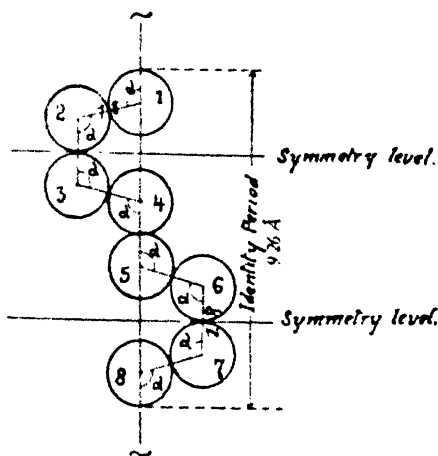


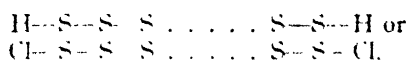
FIG. 1.—Arrangement of atoms in the elastic sulphur.

⁴ *Helv. chim. act.*, 1935, 18, 570.

temperature of 200° , on heating virgin sulphur. If cooled still further, it slowly liquefies; on heating thereafter, it quickly becomes viscous, but never acquires the high viscosity of heated "virgin" sulphur.

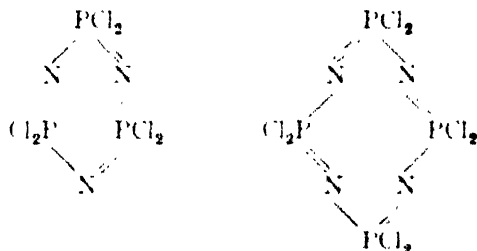
Hence it would seem that, at high temperatures, the long chains break up into a large number of shorter chains, which are more stable than the long chains of "virgin" sulphur. Possibly, in the process of cooling, they leave behind such a large number of nuclei that on re-heating a large number of short chains are formed instead of a small number of long ones.

The viscosity of highly viscous sulphur is greatly diminished, by addition of traces of halogen or of hydrogen-sulphide; at the same time, the amount of S_8 in the equilibrated mixture becomes smaller. We think that shorter chains with Cl, Br, I or H at the ends are formed:



These phenomena show that the polymerisation of sulphur is to be regarded as similar to that of other reactions of polymerisation.

The second elastic substance is polyphosphonitrilic chloride, discovered by Stokes,⁵ which is produced by heating various phosphonitrilic chlorides of low molecular weights, namely, the annular compounds:



Polyphosphonitrilic chloride is almost indistinguishable, externally, from slightly-vulcanised rubber. Under tension it develops a double retraction and yields a fibre diagram, as Pankow⁶ has discovered. This diagram shows a fibre period of 5.17 \AA , and in the direction of the fibres a diagonal screw axis. The most probable arrangement of the P and N atoms is shown in Fig. 2, which is based upon the X-ray diagram, the diameters of the P and N atoms and the angles known from compounds such as POCl_3 and NH_3 .

Here again, like in sulphur or stretched rubber, long chains of primary valency are arranged parallel to the direction of tension. The space of one identity-period in the axis is occupied by two PNCl_2 residues. When the tension is withdrawn, the interferences disappear. Cooling in the tense state causes the crystallised state to "freeze stiff," as in the case of rubber or fibrous sulphur.

We have also plotted the load-extension curve of this inorganic rubber. Phenomena of plastic flow are superposed on the phenomena of elastic deformation; on the whole, this curve resembles that of rubber. We have investigated them with reference to the temperature-tension curve of a stretched test piece, and the curve is also wholly analogous to that of rubber (Fig. 3).

⁵ *J. Am. chem. Soc.*, 1895, **17**, 275; 1897, **19**, 782.

⁶ *C. r. de la Soc. phys. et hist. nat. de Genève* (Juillet, 1935).

On heating, at a constant degree of deformation, the tension increases, and more than would be proportionate to the absolute temperature. The reason is that crystallised portions "melt" and also undergo tension. On cooling, the tension remains at first higher than in the process of heating and decreases proportionately to temperature; it gradually continues to decrease also at constant temperature. The substance enters at first into the amorphous "under-cooled, metastable state," and crystallisation and the restoration of the original degree of tension takes place only gradually.

Definite information as to the mechanism of contraction can be drawn from this temperature-tension curve. Contraction is produced, not by the action of attractive forces, but by the thermal agitation of

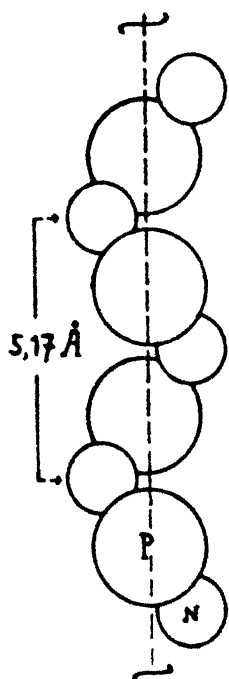


FIG. 2.—Probable arrangement of the P and N atoms in polyphosphonitrilic chloride.

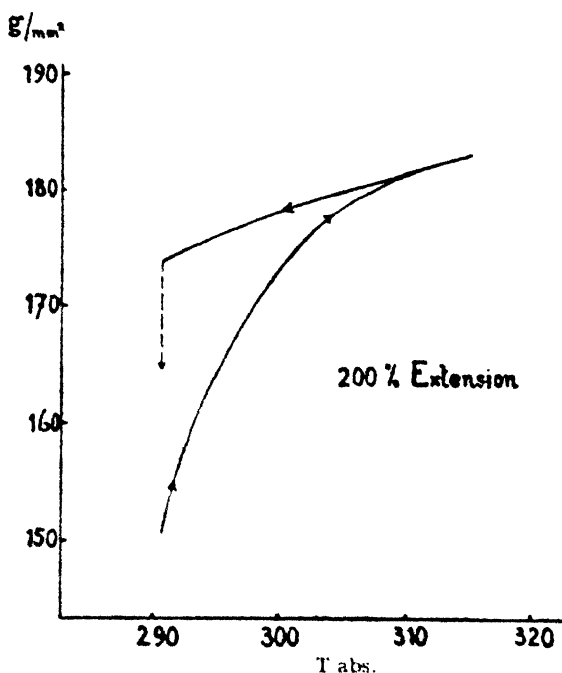


FIG. 3.—Stress-temperature curve of $(N)P(Cl)_2$ at 200 per cent. extension.

the links of the flexible chains, which tends to produce the statistically preferred condition in which the chains are completely *disorientated*, in comparison with the less probable *orientated* arrangement.*

We are not as yet in a position to make any statement on the kinetics and the equilibrium of the polymerisation of $(PCl_2N)_n$. Henmi has found, however, that the reaction is reversible—depolymerisation sets in slowly at low temperatures under the influence of specific chemicals, such as dioxane. A mixture of the phosphonitrilic chlorides of lower molecular weights is thus obtained.

The same considerations apply here as in the case of sulphur. If

* Cf. the theory of elasticity of rubber given by Meyer, Valko and Ferri, *Kolloid. Z.*, 1932, **59**, 208; *Helv. Chim. acta*, 1935, **18**, 570.

endothermic polymerisation is to be possible, the atoms or groups of atoms in the polymeric product must have a greater phase-volume—*i.e.*, greater mobility—than in the rigid annular trimer or tetramer. Hence the chains must be flexible.

It will be seen that there are strong analogies between the two inorganic and highly polymeric substances and the organic polymers, both in the morphological arrangement of the atoms and in the manner of their polymerisation.

GENERAL DISCUSSION

Dr. R. Houwink (*Eindhoven*) said: Is there an explanation of the recent observations of Sakurada and Erbring⁷ on the change in tensile strength of stretched elastic sulphur threads with time. If the observations of these authors are corrected so that the tensile strength is calculated on the actual area during the test, it is, *e.g.*, found for a sulphur, prepared at 300° C., that the strength firstly decreases within two days from 720 to 282 kg. mm.⁻², then it increases within four days to 1160 kg. mm.⁻² again, after which period it starts to decrease steadily as a consequence of the transition $S_n \rightarrow S_8$. If the rise from 282 to 1160 kg. mm.⁻² could be ascribed to an increase of the chains in the weak rubbery mass, to what cause may then the initial decrease be ascribed?

Professor K. H. Meyer (*Genève*), in reply to a question of Dr. Katz suggesting that there is a close connection between extensibility and the phenomenon of crystallisation on stretching (Katz-effect): One can easily understand that crystallisation occurs only, and only can occur, if the chains are built up in a regular way, like sulphur chains or natural rubber chains. If the chains are irregular (as in some natural protein chains, *e.g.*, the elastic ligament (*ligamentum nuchae*) or chains of so-called synthetic rubber, which is a very irregular and branched hydrocarbon), then we observe *extensibility*, but no *crystallisation*.

One can prevent rubber from crystallising by vulcanisation with a sufficient quantity of sulphur, so as to make the chains irregular.*

Referring to the theory of Mack,⁸ who explains the contraction of rubber by forces of attraction which are saturated during contraction, I say most definitely, that this theory is in contradiction with the important phenomenon of the Gough-Joule-effect and therefore cannot be seriously taken into account. A saturation of forces or "condensation" would involve *evolution* of heat during contraction, while *absorption* of heat is observed.

As to the form of the molecule of sulphur in the liquid state, I can only say that the enormous rise in viscosity during production of the elastic form clearly indicates a polymerisation in the molten state.

Mr. Houwink speaks of the peculiar behaviour of freshly prepared elastic sulphur: the tensile strength first rises, and then falls. There are certainly several reactions, which by superposition can cause maxima or minima. Elastic substances, when heated and cooled, undergo a change in the molecular arrangement of the chains, a sort of partial "crystallisation," by which the solubility is augmented. This fact is well known with rubber, which shows different load-extension curves when it has been previously heated or when kept for some time at ordinary temperature. On this phenomenon is superposed, in the case of sulphur the depolymerisation, which diminishes the tensile strength.

* Koll. Z., 1935, **74**, 129.

⁸ *Helv. Chim. acta*, 1935, **18**, 570.

⁷ *J. Am. Chem. Soc.*, 1934, **56**, 2770.

KINETICS OF RING-FORMATION AND POLYMERISATION IN SOLUTION.

By G. SALOMON.

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In a series of experiments carried out by H. Freundlich¹ and his co-workers, the kinetics of the reaction



were investigated by measuring the increase of the halogen ion concentration, and the reaction was found to be strictly of the first order. The velocity of the reaction was not influenced catalytically by the presence of neutral salts, and impurities in the starting material were inactive. In aqueous and aqueous-alcoholic solution, it was necessary to use excess alkali, but this was merely to neutralise the halogen acid set free; apart from this, the reaction velocity was, within wide limits, independent of the (OH^-) concentration. The reaction also takes place in anhydrous organic solvents, but with a much smaller velocity.

Fig. 1 shows what great differences were observed by Freundlich and his co-workers in the velocity of formation of various rings. The 5-ring is formed 100,000 times quicker than the 4-ring. At first there was no theoretical explanation for this extremely small tendency of formation of the 4-ring; Ruzicka³ had

found similar results in synthetical experiments, and he recognised a general regularity in intramolecular ring closures. The 4-membered ring is very easily formed by a bimolecular reaction, and Ruzicka attributed the very small tendency to formation in the intramolecular reaction to the infrequency with which the ends of the molecule meet, corresponding of course to the higher energy of formation of such strained rings. Actually, however, the circumstances are even more complicated than this, but the theory has been of great value to us² and the subdivision

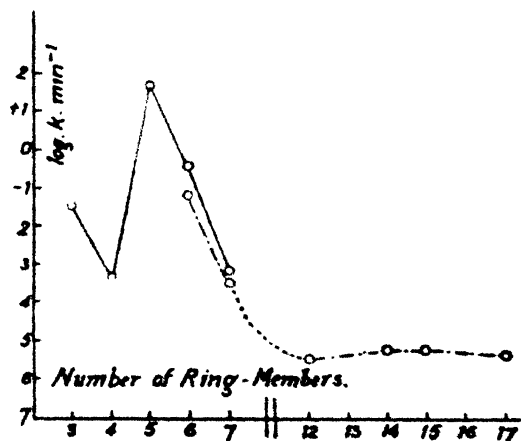


FIG. 1.

— — — Solvent: Water.

— — — — — Solvent: 30 per cent. isopropyl alcohol

¹ Freundlich and co-workers. *Z. physik. Chem.*, 1911-1933. Last part, 1933, 166, 161.

¹ *Helv.*, 1926, 9, 230.

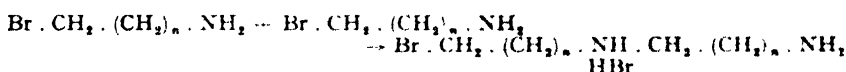
³ Freundlich and Salomon, *Ber.*, 1933, 66, 355.

into energy- and statistical-factors ⁴ soon allowed us to recognise a number of regularities.

Some time ago, Ziegler ⁵ and his co-workers were successful in synthesising many-membered ring systems in dilute solution, and these experiments seemed to us to be a promising basis for the investigation of the reaction kinetics of the formation of cyclic imines with a large number of ring members. Experiments carried out in the laboratory of L. Ruzicka and in collaboration with K. E. Meyer soon led to this goal. As shown in Fig. 1, the ring closure to a many-membered ring in aqueous-alcoholic solution proceeds 50 to 100 times more slowly than the formation of the 4-ring in aqueous solution, and thus differences are known of ring closures under similar conditions which vary in the ratio of 1 : 5·10⁶, depending on the length of the chain. Greater differences than these are recognised when comparing relative rates of formation in organic solvents, and the following figures will afford an example of this.

The period of half-change in the formation of a 5-ring in water from the corresponding bromamine is, at 25°, about one second; in toluene, a few minutes. At the same temperature, and in aqueous alcoholic solution, the half period of formation of a 14-ring is two months, and in toluene thirty-three years. In other words, the synthesis of the higher ring systems must be carried out at a higher temperature.

In contrast to the intramolecular ring closure reaction, the intermolecular polymerisation



is largely independent of the chain length; it is, however, influenced by the solvent, and this circumstance allows us to divide the influence of the solvent into inter- and intra-molecular factors, and to see the specific relation between the ring closure and the solvent. Naturally, the reaction velocity constants of the intra- and inter-molecular reactions are not comparable on account of the difference in the dimensions. On the other hand, the dependence of both reactions on temperature is given by the Arrhenius' equation, and by suitable division of the factors independent of temperature, it was possible to obtain comparable values. This comparison was carried out in the following way.

Theory of Irreversible Ring Closure Reactions.

It is convenient to divide the course of the reaction into three phases:

1. The two ends of the molecule capable of reacting, in our case, halogen alkyl and alkyl amine are moved by thermal impacts of the surrounding molecules, this movement being defined by the links in the carbon chain and the valency angle. There is a definite probability that the ends of the molecule will approach within a distance r , the sphere of molecular activity.

2. The molecules attract one another, and form an intermolecular compound. This compound has a definite life period, and can either revert to the normal open chain compound or it can undergo the third phase of the reaction which is.

3. A thermal reaction resulting in ring formation.

⁴ Cf. Hückel, *Theoretische Grundlagen der organ. Chemie*.

⁵ Ziegler, Eberle and Ohlinger, *Ann.* 1933, 504, 94.

Corresponding to this idea, we can formulate the Arrhenius' equation thus

$$k_1(\text{sec}^{-1}) = Z_1 \cdot e^{-\frac{E_1}{RT}} = P_1 \cdot Z'_1 \cdot e^{-\frac{E_1}{RT}},$$

Z_1 is a value calculated from the temperature function of the reaction velocity and Z'_1 corresponds to the real reaction (phase 3), whilst P_1 represents the probability of the first two phases.

We shall next consider the essential reaction, that is the case when $P_1 = 1$ and $Z_1 = Z'_1$. The velocity of the reaction is determined by formation of halogen ions, or in general by the transition of halogen atoms from inside, to outside, the sphere of action.⁶ The mechanism of the reaction is analogous to numerous bimolecular reactions between halogen alkyl and alkyl amine, but it is also related to inorganic reactions such as the transformation of purpureo-chromium chloride, to roseo-chromium chloride.⁶ This reaction, the separation of a covalent link is an endothermic reaction, and therefore requires an appreciable energy of activation. Recently, M. Polanyi⁷ and his co-workers have given a general scheme for ionogenic reactions. The theoretical calculations of the activation energy of such reactions agree well with the experimental values of 20 to 25 K-Cal. On the other hand, in the formation of 5-6 membered ring systems, generally a smaller energy of about 12 to 20 K-Cal. is found. The latter value is, however, also valid for the analogous bimolecular reaction. A reduction of the activation energy of this reaction is easily explained by the action of the amino group. The halogen ion will, in formation, be attracted by the amino group and the work required for the removal will, therefore, be diminished.

The factor independent of temperature, Z_1 , has the dimensions of a frequency. According to Polanyi and Wigner,⁸ this signifies in large organic molecules the frequency with which the atom or atomic group vibrates about a definite bond. On account of the connection between atom vibration and the Raman and infra-red spectra, this factor must have the value 5×10^{12} - 5×10^{13} sec.⁻¹. According to this theory, therefore, the thermal decomposition of organic molecules is a pre-dissociation phenomenon.

As Table I shows, the theoretical value of Z was obtained in four very different types of ring closure. Other ring closures in aqueous solution (Fig. 3) show values which are smaller by several (1 to 3) powers of ten, but these deviations are easily explained by the closer statistical argument which follows. On the other hand the factor independent of temperature, is found, in organic solvents, to have a value which is 10^5 to 10^7 times too small. Since, on this account the intermolecular reaction also proceeds slowly in organic solvents, the solvent obviously influences the reaction mechanism. On account of the good agreement between the theoretical and experimental values for Z in Table I, it was clear, that water was the natural solvent for such ionogenic reactions and a specific explanation should be sought for the anomalies in organic solvents.

An increase in the value of Z' occurs only in the case of the ring closure of bromo-ethylamine (*cf.* Table I), in which the molecule consists of only three atomic groups in contact one with another. This indicates certain inner degrees of freedom, and therefore the transference of energy

⁶ H. Freundlich and R. Bartels, *Z. physik. Chem.*, 1922, **51**, 177.

⁷ Ogg and Polanyi, *Trans. Faraday Soc.*, 1935, **31**, 604.

⁸ *Z. physik. Chem.*, 1928, **139A**, (Haber volume), 430. O. K. Rice and Ramsberger, *J.A.C.S.*, 1928, **40**, 617.

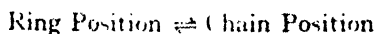
TABLE I.—SOLVENT : WATER.

Halogenalkyl Amine.	Ring.	Z (sec ⁻¹).
Br . CH ₂ . CH ₂ . NH ₂	$\begin{array}{c} \text{CH}_2 - \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{NH} \end{array}$	6.3 . 10 ¹⁴
Cl . CH . CH ₂ . NH ₂ $\begin{array}{c} \diagup \\ \text{C}_6\text{H}_5 \end{array}$	$\begin{array}{c} \text{C}_6\text{H}_5 . \text{CH} - \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{NH} \end{array}$	1.0 . 10 ¹³
Cl . CH . CH ₂ . CH ₂ . CH . NH ₂ $\begin{array}{cc} \diagup & \diagdown \\ \text{CH}_3 & \text{CH}_3 \end{array}$	$\begin{array}{c} \text{CH}_2 - \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{CH}_2\text{CH} \quad \text{CH} . \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{NH} \end{array}$	4.0 . 10 ¹³
Br . CH ₂ . (CH ₂) ₄ . CH ₂ . NH ₂	$\begin{array}{c} (\text{CH}_2)_4 \\ \diagdown \quad \diagup \\ \text{CH}_2 \quad \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{NH} \end{array}$	5.3 . 10 ¹³

is favoured. In the following we shall discuss how far the differences between Z and 10¹³ are caused by the probability of the first two phases.

It is important to define these probabilities. The first phase includes the change of the shape of molecules, which may be influenced by the chain length and may be different in various solvents. The second phase, which brings into question the life period of the intramolecular compound, may vary with the experimental conditions, *e.g.* with variation of the dielectric constant of the solvent and its hydrostatic pressure. In contrast, the third phase, the real reaction, should be affected only by the predissociation phenomenon; it is defined by the potential surfaces of the molecule. As the probability as to the first or second phase will be varied in our experiments, we shall discuss in this paper the *a priori* probability of these two phases.

If the active ends of the molecule approach to within the distance r , then the mutual attraction of the two groups will overcome the thermal forces. If we describe this spatial position as the "Ring Position," and all other possible forms as the "Chain Position," then we arrive at the equilibrium



and the definition may be given

$$P_1^\alpha = \frac{\text{Number of Molecules in the Ring Position}}{\text{Total number of Molecules}}.$$

Thus when $P_1^\alpha = 1$, all molecules are at any time in the ring position. On the other hand when $P_1^\alpha = 0$, it indicates that the ends of the molecule never approach to within the distance r . Let the average most probable distance of the molecule ends (in the normal position of the chain) be R . Then the value of P_1^α is determined by the ratio $r : R$ and the number of the possible transformations from the normal position to the ring position.

R certainly increases with increasing length of the carbon chain. By considerations based on the study of models it is seen that the value

of R increases very rapidly, and the ratio of $r : R$ becomes progressively smaller and finally reaches the limiting value of zero. This would lead one to think that there would be great differences in the ease of formation of the many membered rings, for instance between the 15- and 17-ring, and between the 30- or 32-ring. Ziegler's experiments have shown that this is not the case, and he has already pointed out the contradiction between experiment and theories based on models. The reason of the contradiction is probably as follows.

Long chain molecules are in constant Brownian movement,⁹ and to this may be ascribed the magnification of the Eötvös constant in the case of the higher fatty acids.¹⁰ Solutions of long chain compounds show for this reason, large anomalies in their osmotic behaviour.¹¹ It appears, therefore, that we should also ascribe to short chains a certain inner Brownian movement, and the vibration of the individual members of the chain one against the other renders the completely closed and the fully extended form equally improbable. Entropy considerations¹² indicate the half-closed form as the most probable, and if this is the case, then the introduction of another member into the carbon chain will increase the average distance R between the ends of the chain only by a small quantity, and R will tend to reach a limiting value.

The probability of ring closure will be governed by the condition of the valency angle, as the chain might frequently be in the necessary spatial position for ring closure, which can only occur if the position of the valency angle is correct. This "steric hindrance" of the valency angle distinguishes the 5-membered ring from all the others. The movement of the 5-membered chain takes place chiefly in a plane, and the three possible plane configurations predominate.

These three forms may be mutually converted, one into the other, or into the ring position, which is a contrast to the many spatial forms of the 6-, 7-, 8-membered chains. In longer chains this factor is of little importance as, on account of the great number of degrees of freedom, many of the spatial forms can be converted into the ring form.

Formerly it was assumed that all geometrical isomers were equally probable, but the Raman spectra of 3-, 4-, and 5-membered chains points

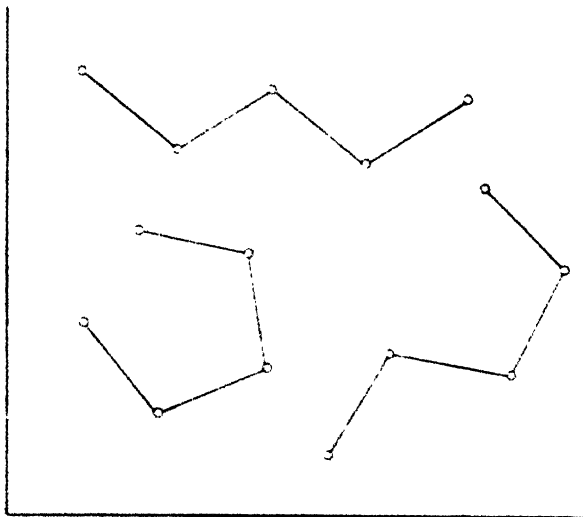


FIG. 2.

⁹ Born and Courant, *Physik. Z.*, 1913, 14, 731. Madelung, *ibid.*, 1913, 14, 729.

¹⁰ Freundlich, *Kapillarchemie*, 1930, 1, 53.

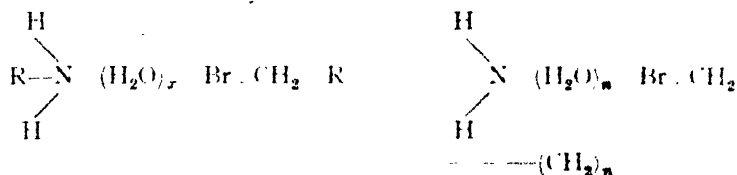
¹¹ K. H. Meyer and Lohdemann, *Helv.*, 1935, 18, 307.

¹² Guth and Mark, 1934, *M.* 65, 93. W. Kuhn, *Kolloid Z.*, 1934, 68, 2.

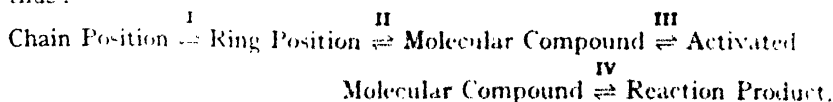
to the existence of at least two favoured forms.¹³ Interatomic forces cause a limitation of the freedom of rotation¹⁴ and individual geometric forms are favoured. According to Kohlrausch no characteristic Raman line for the ring configuration could be observed, as it is obviously hindered on statistical grounds, and the results of kinetic investigations are in harmony with this conclusion. For the 5-membered ring $0.03 > P_1^a \leq 0.01$. According to Fig. 2, however, every third molecule should be in the ring position, i.e. $P_1^a = 0.3$, and according to this the 5-ring occurs 10 to 30 times more seldom than would be expected on purely statistical grounds.

The first kinetic problem with which we have to deal is to prove qualitative agreement with the theory of the diminishing value of Z with increasing length of chain. It might be considered that only a few ring systems are what might be called "normal." What statistical circumstances would be met with in the strained 3- and 4-membered rings cannot be predicted, but even rings with a medium number of members—9 to 14—are anomalous. According to Ruggli,¹⁵ J. v. Braun,¹⁶ Ruzicka,¹⁷ and Ziegler,⁵ they are certainly difficult to form and Carothers¹⁸ showed that they are extremely unstable when formed. Here we probably have the steric hindrance of the valency angle together with the hypothetical steric hindrance of the molecular structure itself.¹⁹ These factors must therefore be added to the already complicated statistical circumstances.

Before discussing experimental results, the general influence of solvents on the speed of reaction should be referred to. Inter- and intra-molecular reactions result in the formation of molecular compounds in which the reactions finally occur.



The phase of the reactions which leads to this molecular compound is the only one affected by the difference in dimensions. Opposed to the simple ionogenic theory there is the additional restriction in both the complexes of the action of the amino group. In the sense of the theory of Polanyi and Wigner, no more than the energy with the frequency of 10^{13} is necessary to overcome the C—Br linkage, but at the same time it must fulfil any restrictions there may be between $^{20} \text{CH}_2\text{Br-solvent-NH}_2 \cdot \text{CH}_2 \text{---}$. On account of this simultaneity the life period of the molecular compound will be real. The reaction consists, as it were, of a series of equilibria, thus:



¹³ K. F. W. Kohlrausch, *Z. physik. Chem. B.*, 1932, **18**, 61. K. F. W. Kohlrausch and Köppel, *ibid.*, 1934, **26**, 209. *M.* 1935, **65**, 185.

¹⁴ Eucken and Weigert, *Z. physik. Chem. B.*, 1934, **23**, 265.

¹⁵ Ruggli, *Ann.*, 1912, **392**, 92; *Ann.*, 1913, **399**, 175.

¹⁶ J. v. Braun, *Ber.*, 1906, **39**, 4110.

¹⁷ *J. Am. Chem. Soc.*, 1929-1935; cf. J. v. Braun and co-workers, *Ber.*, 1924,

57, 185.

¹⁸ M. Stoll and G. Stoll-Comte, *Helv.*, 1930, **13**, 1185.

²⁰ H. Eyring, *J. Chem. Physics*, 1935, **3**, 107.

Actually, the life period of the molecular compound in water is long. Only the equilibrium I (the steric factor) and III (activation energy) will then determine the velocity. In pure organic solvents on the other hand, the speed of reaction diminishes in the series nitrobenzene, acetophenone, benzyl alcohol, methyl alcohol, halogenated hydrocarbons, benzene, xylene, decalin. This series is in agreement with that which has been found for similar bimolecular reactions.²¹

There seems therefore to be a connection between the hindrance of the reaction, the ionisation process and the dielectric constant of the solvent, but this assumption is not sufficient. There is a non-ionic reaction which is slowed by the solvent, namely the association of free radicals,²² $2(\text{C}_6\text{H}_5)_3\text{C}\cdot \rightarrow (\text{C}_6\text{H}_5)_3\text{C}:\text{C}:\text{C}:(\text{C}_6\text{H}_5)_3$. There exists, according to Ziegler, a relationship between radical formation and spatial packing.²³ If the radical has a high density, then the work of the association must be performed against the solvent, and the association will, therefore be hindered. Correspondingly in the amine reaction the molecular compound has perhaps a favourable spatial packing in polar solvents, and therefore the life period is increased. With increasing symmetry of solvent, the molecular compound finally reaches its normal life period, which consequently determines the rate of the reaction. The fact, therefore, of the solubility in organic solvents of the imine salts, which closely resemble the molecular compounds, is in some degree related to the speed of the reaction.^{24, 25} To separate the influence of the solvent from the geometric factor P_1^a , we use a second probability factor, P_1^b , which is defined as follows:

$$P_1^b = \frac{\text{Number of non-activated molecules in the molecular compound}}{\text{Number of molecules in the ring position}}$$

and in aqueous solution P_1^b is 1.

For the intermolecular reaction we have the Arrhenius' equation

$$K_2 (\text{sec}^{-1} \text{ mol. } L^{-1}) = Z_2' e^{-\frac{E_2}{RT}} = P_2 \cdot Z_2' \cdot e^{-\frac{E_2}{RT}},$$

Z_2' gives directly the frequency of collisions. The value of Z_2' depends on the mass and radius of the molecule, and is of the order of magnitude of 10^{11} ($\text{sec}^{-1} \text{ mol. } L^{-1}$). A certain correction is necessary for the viscosity of the solvent, but this does not affect the order of magnitude of Z . The probability factor P_2 can again be divided into two components, the geometric factor and the influence of solvent P_2^a and P_2^b respectively. P_2^b may be defined as follows:

$$P_2^b = \frac{\text{Number of non-activated molecules in the molar compound}}{\text{Number of collisions}}$$

The two values of P^b make it possible to compare the influence of the solvent. The geometric structure of the chain plays scarcely

²¹ Moelwyn-Hughes, *The Kinetics of Reactions in Solution*, Oxford, 1933.

²² The hindrance of the reaction is calculated according to the measurements of Ziegler and co-workers, *Ann.*, 1929, 473, 163; 1933, 504, 131.

²³ *Trans. Faraday Soc.*, 1934, 30, 10.

²⁴ In this connection it would be essential to know the behaviour of the bimolecular reaction in water. This had not hitherto been investigated on account of the slight solubility of the halogen alkyls in water. For this investigation, the reaction $\text{R}_2\text{N} + \text{Cl} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_2 \rightarrow \text{R}_2\text{N} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_2$ would be especially suitable, since the formation of 4-membered rings proceeds very slowly between 0° and 36°.

²⁵ Cf. Soper and Williams, *Trans. Chem. Soc.*, 1931, 2291.

any role in the bimolecular reaction, and as a matter of fact it is found that in a number of bimolecular reactions the length of the chain is without effect.²⁶ If, however, anomalies should appear, then we must consider that the extended chain form, in which the active groups are available from all sides, favours polymerisation, which is the direct opposite of the conditions for ring closure. In general the assumption that $P_2^\alpha \cong 1$ is sufficient.

Shape of Chain Molecules and Solvent.

The statistical proportions encountered in the formation of imines are shown in Fig. 3.²⁷ The *a priori* probabilities for ring closure in water

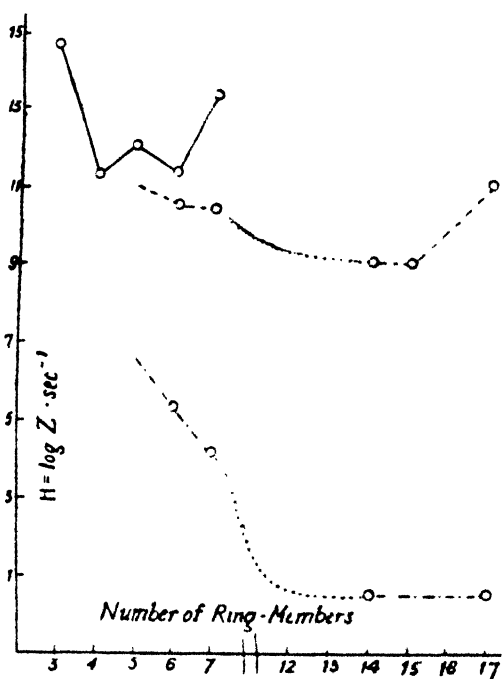


FIG. 3.

— Solvent: Water.
 - - - 30 per cent. isopropyl alcohol.
 . . . Xylene.

the dissolved molecule will naturally favour the form with the smallest energy content, *i.e.* that form which presents the smallest surface area to the solvent. This means the ring position. In capillary active solvents, on the other hand, the surface forces are small in comparison with kT , and here the true statistical ratio is obtained. In xylene the correct sequence is found, and it behaves here with the relative ease of formation for the 6 : 7-rings of 10 : 1.

²⁶ Moelwyn-Hughes, *loc. cit.*, ²¹, p. 91.

²⁷ The measurements for the 3-6 membered rings are largely drawn from the work of Freundlich, and are fully discussed in *Helv.*, 1933, 16, 1361. Exact measurements for the 7-ring in water, *Helv.*, 1934, 17, 851. The individual data for all other measurements are unpublished.

Now, are the surface forces between brom-hexyl-amine and water sufficient to bring about the kinetic anomalies observed? Langmuir²⁸ has shown how such differences of energy between the molecular forms can be calculated. He applied the known data of surface chemistry to the solution of the problem, and calculated the surface forces between water and a monocarboxylic acid in the cylindrical and the spherical form, and found the values shown in Table II.

TABLE II.

Acid.	Energy in ergs $\times 10^{-14}$ Cylinder.	Sphere.	λ .	P_A .
C_3H_7COOH	46	40	6	4.5
$C_{14}H_{29}COOH$	208	139	69	3×10^7

The energy difference λ determines the ratio of the *a priori* probabilities of the two forms: $P_A = e^{-\lambda/kT}$, at ordinary temperatures kT amounts to 4×10^{-14} erg. Whilst with butyric acid the spherical form prevails over the cylindrical form only by 5:1, in palmitic acid the molecules are entirely in the cylindrical form. For an acid C_nCOOH , $\lambda \approx 15$ to 25×10^{-14} erg per molecule, which gives the corresponding value of P_A as $10^{-1.6}$ to $10^{-2.7}$. As Fig. 3 shows, the probability of the formation of a 7-ring in water becomes 10^3 to 10^4 times larger. Thus with the help of this very crude comparison with the carboxylic acids, we reach the correct order of magnitude in the effects sought for.

For the exact application of Langmuir's method to the halogen-alkylamines, a great deal of physical data are lacking. Moreover, although the ring position considered here is similar to the spherical position of Langmuir, it is not identical with it. Correct orders of magnitude can be obtained, however, by comparing the compounds

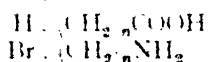


TABLE III—SOLUBILITY IN MOLES PER LITRE AT ROOM TEMPERATURE.

n .	$H-(CH_2)_nCOOH$ in Water.	$Br-(CH_2)_nNH_2$ in Water.	$Br-(CH_2)_nNH_2$ in 10 Per Cent. Iso- propyl Alcohol.
4	0.3	—	—
5	0.084	0.8	—
6	0.016	0.004	2.0-2
8	$7 \cdot 10^{-4}$	—	—
11	—	$< 1 \cdot 10^{-8}$	0.003
13	$\sim 5 \cdot 10^{-7}$	$< 1 \cdot 10^{-7}$	0.001
16	—	$< 1 \cdot 10^{-8}$	< 0.001

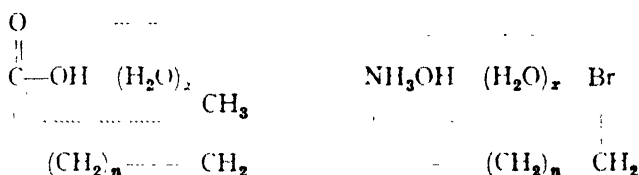
that of the CH_2Br group is larger than that of the CH_3 group. Now according to Langmuir,²⁹ there exists a close relationship between solubility and capillarity, and, if the comparison is correct, the solubility of the alkylamines must be of the correct order of magnitude.

The fact is that the solubilities of the halogen alkylamines up to C_8 are considerably larger than those of the corresponding carboxylic acids,

²⁸ *Colloid Chemistry*, by S. Alexander, New York, 1926.

²⁹ *Colloid Symposium*, III., 1925.

but in the transition from C_5 to C_6 the solubility sinks to a fourth in the carboxylic acids, whilst with the halogen alkylamines it falls to 1/200th of its value. The higher alkylamines have a very much smaller solubility, even in 10 per cent. isopropyl alcohol. This rather sudden change of solubility is simultaneous with the occurrence of the anomalous behaviour observed, and with the preponderance of the spherical form of the molecule. One may, therefore, suppose that the phenomena are related. In contrast to the carboxylic acids the halogenated amines can change into an inner molecular compound



In this molecular compound the actions of the hydrophilic groups are gradually mutually saturated, and in consequence of this, the action of the hydrophobic groups becomes stronger and the compound becomes insoluble in water. As long as the solvent has only a small effect on the molecular structure, the open chain form will remain in water, but if the spherical form is enforced by the solvent, then the more sparingly soluble molecular compound is formed.

If we take, on the one hand, the *a priori* probabilities found in benzene and xylene for the 6:7-ring = 10:1, and on the other hand, the observed solubilities, then the following values are probable (Table IV.).

TABLE IV.

Ring.	$Z_1 \text{ sec.}^{-1}$.	P_1^a .	$\lambda 10^{14}$ Erg Per Molecule.	P_λ .	P_1^a , Corrected.	Relative Frequency of the Ring Position.
5	$1.0 \cdot 10^{12}$	0.03	5	3.5	0.01	250
6	$2.5 \cdot 10^{11}$	0.005	10	10	0.0004	10
7	$2.5 \cdot 10^{13}$	0.5	40	25,000	0.00004	1

As can be seen it is necessary to make only relatively small proportional corrections for the 5- and the 6-ring to make the differences of the *a priori* probabilities appear six times larger. The assumption of a rather sudden increase in the value of λ for the 7-ring depends only on the observed insolubility, and this assumption was successfully proved with the aid of a kinetic method.

It is well known that the addition of a small quantity of a capillary active substance lowers the surface tension of water in a very characteristic manner, and this phenomenon depends on a change in the structure of the surface. Now, if there is a relation between the capillary activity of a solvent and the shape of molecules, then a change in the capillarity of the solution (not the surface) must influence not only the shape but also the *a priori* probability of reaction. The larger the value of λ , the larger this effect must be, and this is, as a matter of fact, the case.

The addition of only 10 per cent. isopropyl alcohol is sufficient to

TABLE V.

Reaction.	$\text{Cl}(\text{CH}_2)_6 - \text{NH}_2 \rightarrow (\text{CH}_2)_6 > \text{NH} \cdot \text{HCl}.$						$\text{Br}(\text{CH}_2)_6 - \text{NH}_2 \rightarrow (\text{CH}_2)_6 > \text{NH} \cdot \text{HBr}.$						
Solvent.	k 35°	E	$\Delta E.$	$H_{\text{sec.}}$	$\Delta H.$	$P_1^a.$	k 35°	k 74°	E	$\Delta E.$	$H.$	$\Delta H.$	$P_1^a.$
	Relative.	(K-cal.).					Relative.		(K-cal.).				
Water	100	20.9	---	11.4	---	0.005	100	100	24.9	---	13.4	---	0.5
10 per cent. Iso-propyl alcohol	60	---	---	---	---	---	50	22	20.1	4	9.7	3.6	0.0001
30 per cent. Iso-propyl alcohol	24	19.8	0 ± 0.6	10.1	1	0.00025	22	10	20.7	± 0.6	9.8	---	---
60 per cent Methyl-alcohol	17	20.2		10.2		0.0003	---	---	---	---	---		
90 per cent. Methyl-alcohol	5	20.8		10.3		0.0004	---	---	---	---	---		
99.9 per cent. Methyl-alcohol	6	~ 21		~ 10									

lower the rapidity of formation of a 6-ring nearly by half, and with 30 per cent. alcohol the velocity is only a fourth of the velocity in water. After this, the addition of larger quantities of alcohol results in smaller decreases of velocity, until in 90 per cent. alcohol the value is one-tenth of that in water.

Thus the experimental values determined correspond with the calculated values of the *a priori* probability determined in Table IV. The good agreement of the figures is of course accidental. Effects of an entirely different order of magnitude are encountered in the formation of the 7-ring; here the addition of 10 per cent. alcohol is sufficient to reduce the *a priori* probability more than a thousand times; this becomes apparent by a decrease of ΔH of about 3.6. Correspondingly the solubility is very much increased. Consequently the reaction in 30 per cent. alcohol is only twice as slow. Unfortunately bromohexylamine is very difficultly accessible and the experiments in this direction could not be continued, but the foregoing experiments are sufficient to indicate the relations between shape of molecules, solubility and the velocity of reaction.

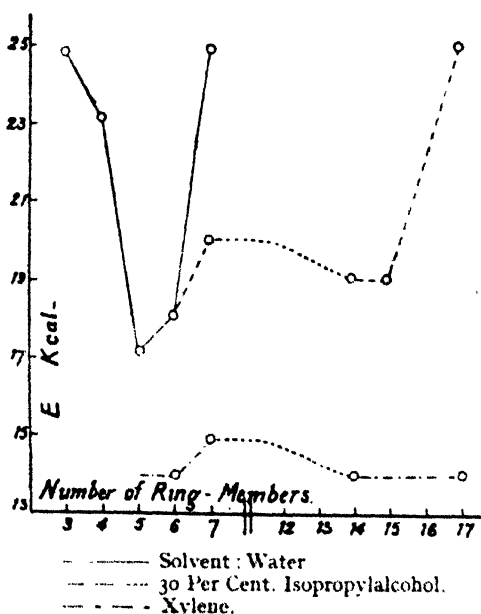


FIG. 4.

The energy of activation of the reaction is also closely bound up with the insolubility. Whilst the value of E remains constant in the formation of the 6-ring in water and in aqueous alcohol, it falls in the formation of the 7-ring about 4 K-Cal. The formation of the 7-ring from the bromamine in aqueous alcohol requires only 2 K-Cal more energy than the formation of the 6-ring in this solvent. This latter difference also obtains in benzene and is probably closely connected with the steric hindrance and the structure of the molecule. According to Polanyi, the larger the ionic radius of the halogen ion (in the nascent state), the larger will be the work of separation. The somewhat sudden increase in the energy of activation in water depends also on the formation of a hydrated sheath on the amino group. Freundlich³⁰ and his co-workers have found that certain ring closure reactions proceed not only in organic solvents but also in charcoal, with an activation energy of 4 to 5 K-Cal. less.

The exact investigation of the temperature coefficients of these reactions shows how inaccurate conclusions drawn solely from the velocity constants can be. The small rate of formation of the 7-ring (Fig. 1) in water is due to the large energy of activation, and in organic solvents to the infrequency with which the ends of the molecule approach each other. Similar circumstances obtain in the case of the formation of the 17-ring in aqueous alcohol solution and xylene. Generally the organic solvent favours a smaller activation energy and this would *ceteris paribus* cause a quicker reaction. But on the other hand the solvent is unfavourable to the value of Z , so that the final result is a diminished reaction velocity. In Table VI. a few examples of the influence of solvent are collected.

TABLE VI

Reaction.	$\text{ClCH}_2\text{CH}_2\text{NH}_2 \rightarrow \text{CH}_2\text{CH}_2\text{NH} \cdot \text{HCl}$					$\text{R}_1 \cdot \text{N} \cdot \text{T} \rightarrow \text{R}_1\text{N} \cdot \text{S}_2\text{CH}_3$ and Similar Reactions ($P_2^3 \sim 1$)		
Solvent.	$k_1^{30^\circ}$ Relative	I_1	H	P_1^3	P_1^3	P_2^3	$k_1^{100^\circ}$ Relative	I_2
Water	100	20.0	11.4	0.005	1			
90 per cent. Methanol	8	20.8	10.3	0.0004	~ 1	10^{-4} to 10^{-7}		14 to 16
Nitrobenzene	17	17	7		10^{-3}	10^{-7}		13
Acetophenone	~ 15					10^{-5}	9.7	
Benzylalcohol	~ 10					10^{-6}	10	14
Tetrachlorethane, satt. with water	20	14.5	6.1	constant	5×10^{-5}	10^{-7} to 10^{-8}		12 to 13
Benzene, satt. with water	0.5	15.2	5.0		7×10^{-6}	10^{-8} to 10^{-9}		
Toluene	0.3	16.6	5.8		3×10^{-6}	10^{-7}	0.2	11 to 12
Xylene	0.15	16.8	5.7		3×10^{-6}		0.2	
Hexane	< 0.005			↓			0.01	
Decaline	< 0.005							

If the energy differences between the C_6 chain and water are small, then the diminution of the value of $H + \log Z$ in organic solvents shown in Table VI. can certainly not only be explained by capillary

³⁰ Freundlich and Juliusburger, *Z. physik. Chem. A.*, 1930, **146**, 321. Freundlich and Salomon, *Z. physik. Chem. A.*, 1933, **166**, 179.

chemical effects. For this a value of $\lambda = 30$ to 40×10^{-14} erg per molecule would be necessary and this can in no wise be expected according to Tables I. and III. This consideration is naturally valid only for small chains. In long chains such as C_{16} , λ may be greater than kT in alcohol and in nitrobenzol. In Table VI. the general effect of the solvents on P_1^β is set out and it may be compared with a few values of P_2^β for similar bimolecular reactions,²¹ whereby the impression is obtained that the hindrance by the solvent is even greater in bimolecular reactions. If the intra- and inter-molecular compounds have equal life periods, the ring closure reaction is favoured. In these the energy of the whole molecule can overcome the C-Br link, whilst in bimolecular reactions only the atomic vibration in the halogen-alkyl molecule is active. The differences between P_1^β and P_2^β confirms that the life period of the molecular compound is diminished in organic solvents.

If we consider that to a first approximation the general solvent influence on the factor P_1^β is independent of the length of the chain, then the influence of the solvent can be completely taken into account. By com-

TABLE VII.

Ring.	5.	6.	7.	14-17.
P_1^β	0.61	0.00004	0.000004	$\sim 8 \times 10^{-9}$
Relative probability	1.3×10^6	5×10^4	5×10^3	~ 1

paring the theoretical results of Table IV. with the experimental results of Table VI and Fig. 3, we can obtain both the absolute value for P_1^β and the relative probability of ring closure.

In the transition from the 5- to the 7-ring the *a priori* probability falls by more than 2 powers of 10, and by increasing the length of the chain by a further 7 to 10 members the probability falls again by 3 to 4 powers of 10. The first step fall depends as already explained on the transition from the plane to the spatial forms. The velocity of the reaction shows even greater differences, which are attributable to small differences of activation energy.

The many-membered rings have in xylene at 128° a period of half-completion of three months, and therefore in this case only the order of magnitude of the temperature function can be ascertained. More minute differences between 12-, 14-, and 17-rings would be known from a study of the reactivity of the iodine derivatives, but an objection must be raised here to the value of very exact measurements which attempt to indicate very minute differences. From the temperature function of the reaction the mobility of the molecule can be determined. Now the mobility of the molecule itself and the spatial packing of the solvent are dependent on temperature, and these temperature functions can greatly distort the kinetic data. It would be much more rigorous to measure the temperature coefficient of the reaction velocity at constant volume and not at constant pressure.

It might be expected that in the preparation of the large rings in aqueous alcohol, very complicated circumstances would be encountered. For reasons which will be explained in the next section, only the order of magnitude of the values given in Figs. 3 and 4 for this solvent is correct.

²¹ Moelwyn-Hughes, *loc. cit.*,²¹ pp. 107 and 111.

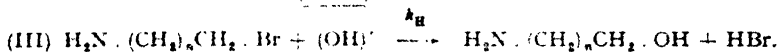
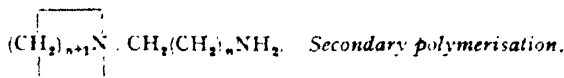
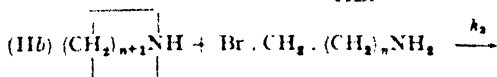
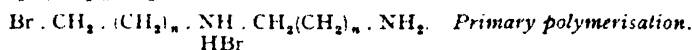
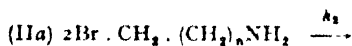
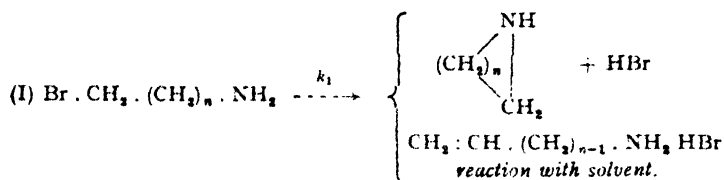
One can see, however, that the *a priori* probability for the formation of a 17-ring in 30 per cent. isopropyl alcohol is not essentially different from that for a 7-ring. It is merely that the C_{16} chain is very insoluble in this solvent. (Solubility in 30 per cent. ethyl alcohol is only 0.002 mol./litre.) The energy differences between aqueous alcohol and the C_{16} chain are essentially larger than with C_5 or C_6 , so that the ring position will be favoured. Corresponding to the 7-ring in water, the preparation of the 17-ring in aqueous alcohol requires an anomalous energy of activation, which anomalous value is not met with in xylene solution. In the formation of the 15-, and 14-rings in the same solvent, smaller probabilities of formation are encountered. This can be connected just as well with the higher solubility and therefore greater mobility of the chain as with a steric hindrance of the reaction.

Whilst a transition from 30 to 10 per cent. alcohol in the preparation of the 6- and 7-rings results only in doubling the velocity of the reaction, the formation of the 12-ring in 10 per cent. aqueous alcohol at 73° is 4 to 5 times quicker than in 30 per cent. alcohol. This change corresponds roughly to the effect caused by a transition from 10 per cent. alcohol to water in the formation of the 7-ring at 74° . Correspondingly the solubility of C_{11} in 10 per cent. isopropyl alcohol is as small as the solubility of C_6 in water (Table III.) Thus we may summarise what is known: the solubility goes parallel with the capillary chemical influence of the solvents on the arrangement of the molecule, and therefore also on the reaction velocity. This relation between the hydrocarbon chain and the solvent is characterised by λ values of the same order of magnitude. It will be remembered that these λ values determine the energy differences between the cylindrical and spherical shape of one molecule in a capillary inactive solvent. The following table of isocapillary forces between chain and solvent can be drawn up:

CH_2 -groups	5.	6.	11.	16.
$\lambda \times 10^{14}$ erg molecule.				
10	$\frac{Br(CH_2)_5NH_2}{\text{water}}$	$\sim \frac{Br(CH_2)_6NH_2}{10\% \text{ isopropyl alc.}}$	$\sim \frac{Br(CH_2)_{11}NH_2}{30\% \text{ isopropyl alc.}}$	$\sim \frac{Br(CH_2)_{16}NH_2}{90\% \text{ alc.}}$
40	-	$\frac{Br(CH_2)_6NH_2}{\text{water.}}$	$\sim \frac{Br(CH_2)_{11}NH_2}{10\% \text{ isopropyl alc.}}$	$\sim \frac{Br(CH_2)_{16}NH_2}{30\% \text{ isopropyl alc.}}$

Methods and Results of Kinetic Analysis.

The synthesis of the large cyclic imines in homogeneous solution is affected by a number of secondary and side reactions. Beginning with the fact that every bimolecular reaction is dependent on concentration, whilst the ring closure reaction is entirely independent of concentration, it was possible by kinetic analysis to work out the conditions favourable for the synthesis. With a few grams of starting material it was possible to obtain quantitative relationships and by combining the figures so obtained with the results of a few preparative experiments, the causes and extent of the disturbances can be almost completely explained. The course of the analysis is as follows:—



The reactions of group (I) are kinetically identical and can only be separated by the investigation of the reaction products. If group (II) represents the main reaction, the concentration of the total amine groups, (primary, secondary and tertiary) remains approximately constant. One obtains reactions of the first order, the velocity of which, in contrast to (I) is still dependent on the concentration of bromamine (A_0). It is best therefore to use a simple graphic method, to find out that concentration in which the reaction velocity is independent of the initial concentration (A_0).

Fig. 5 represents an example of this type of the formation velocity of the 14-ring in aqueous alcohol. In this case the disturbance (II)

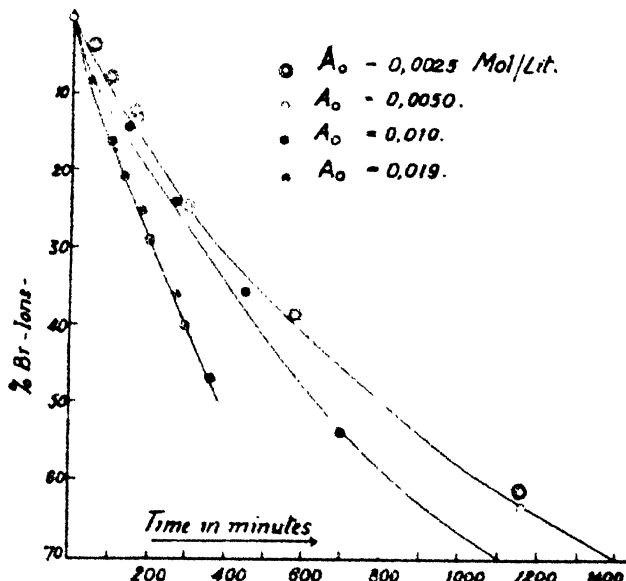


FIG. 5.

Solvent: 30 per cent. isopropyl alcohol. $t = 73.4^\circ$.

falls between $A_0 = 0.0025 \text{ mol./litre}$ and $A_0 = 0.005 \text{ mol./litre}$ within the limits of experimental error. By changing the hydroxyl ion concentration at this dilution the part played by the hydrolysis (III) can be determined very accurately. Now we still have to determine that part of the polymers which fall within the limits of experimental error of the

method. For the primary polymerisation we have

$$dA/dT = -k_1A - k_2A^2 \quad (1)$$

From the known accuracy of measurement and the observed disturbance k_2 is calculated. Since the reaction is observed by the increase of bromo ion and not by the decrease of bromamine, only half of the disturbance which occurs in the expression (IIa) is measured. This is taken into consideration in the calculation of k_2 . For the amount of imine (B) and polymers (D) formed, the following expressions hold:—

$$dB/dT = k_1A \quad (2)$$

$$dD/dT = k_2A^2 \quad (3)$$

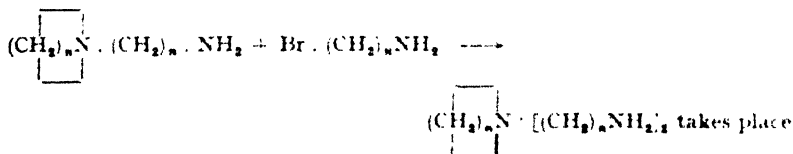
and substituting $k_1/k_2 = f_1$ we obtain from (1) and (2),

$$B = f \ln \frac{f + A_0}{f + A} \quad (4)$$

and from (1) and (3)

$$D = A_0 - A - f \ln \frac{f + A_0}{f + A}$$

For the secondary polymerisation (IIb) no such simple relations hold. Experience, however, shows that the disturbance can be satisfactorily calculated when the decrease of the imino group caused by polymerisation is neglected. This is probably due to the fact that another secondary reaction, namely



If one can therefore treat (IIb) as a disturbance, we have the following

$$dA/dT = k_1A - k_3AB \quad (7)$$

and substituting in (7) $A = A_0 - B$, we obtain a turning-point for the condition $k_3A_0 > k_1$

$$B_{\infty} = \frac{k_1A_0 - k_1}{2k_3} \quad (8)$$

If k_1 is known, k_3 can be calculated from (8). The constant k_3 so derived can be better obtained if some imine is added initially and the disturbance thus increased. It is, however, not possible to determine the proportion of polymers at a definite dilution from k_1 and k_3 . The following equation holds good for the polymers formed here, if we substitute $k_1 : k_3 = g$.

$$A - B = 2g \cdot \ln \frac{g - B}{g} + A_0 \quad (9)$$

The graphic solution, for experimental reasons, does not enter into the matter. On the other hand, an approximate solution is possible, for which I have to thank Dr. V. Weisskopf. If IIb occurs only as a disturbance, equation (9) can be developed according to powers of e and then becomes

$$B = 2\sqrt{2(A_0 - A)g + g^2} - [2g + (A_0 - A)] \quad (9)$$

The yields of monomers calculated with this formula is in good agreement with preparative experiments. The results of the kinetic analysis for one temperature are collected in Table VIII.

TABLE VIII.—SOLVENT: 30 PER CENT. ISOPROPYLALCOHOL; $t = 73.35^\circ$.

Halogenalkylamine.	Ring.	$k_1 \times 10^4$ Min. ⁻¹ .	$k_2 \times 10^2$ Mol. L. ⁻¹ .	$k_3 \times 10^2$ Min. ⁻¹ Mol. L. ⁻¹ .	$k_H \times 10^2$ Min. ⁻¹ Mol. L. ⁻¹ .	$c(k_3)$ Mol. L. ⁻¹ .
Br(CH ₂) ₁₇ NH ₂	17	15	1	~5 (?)	1.3	0.005
Br(CH ₂) ₁₅ NH ₂	15	8	2	9	1.8	0.0025
Br(CH ₂) ₁₄ NH ₂	14	7	2	10	1.7	0.0025
Br(CH ₂) ₁₂ NH ₂	12	4	2	> 20 (?)	1	0.0005
Br(CH ₂) ₈ NH ₂	7	3.30	—	—	—	~0.01
Br(CH ₂) ₃ NH ₂	6	~20,000	—	—	—	∞

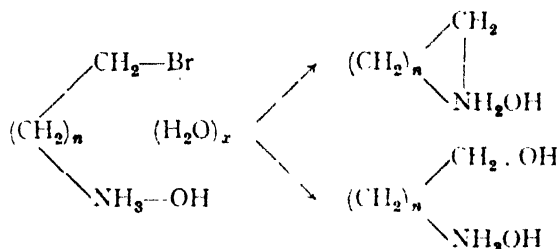
The far greater reactivity of the imines in comparison with those of the bromamines is surprising. Whereas the velocity of formation in the series 17-, 15-, 14-, 12-rings diminishes, the reactivity of the ring formed probably increases, this and the greater reactivity of the imines has a very unpleasant result in the preparations, as the ring formed subsequently polymerises with the unchanged starting material. Contrary to the primary polymerisation, the secondary polymerisation causes only a small increase in the constants of the first order. Thus calculations in agreement with the experimental data show that under conditions represented in Fig. 5, at $A_0 = 0.005$, 40 per cent. and at $A_0 = 0.0025$ mol litre, 25 per cent. of secondary polymers are formed, whilst the deviation of the first order remains small. The limiting concentration given in Table VIII. is related to the secondary polymerisation. At this concentration one observes 25 to 35 per cent. polymers at complete conversion. An essential part of the secondary polymers is formed between the limits of 60 and 100 per cent. conversion, but the weight of the kinetic data is only considerable between the limits of 10 and 70 per cent. conversion.

The measured constants therefore represent infinite dilution in spite of the fact that polymers are formed. By empirical preparative researches, without kinetic analysis of the course of the reaction this particular reactivity of the imino group could not of course be demonstrated. Secondary bases usually have a larger dissociation constant than primary and tertiary. One might suspect a close relationship between the strength of the base and reaction velocity.

The hydrolysis constant $k_H \approx 2 \times 10^{-2}$ corresponds well with that of the more reactive ethyl bromide ($k_H \approx 7 \times 10^{-1}$) at this temperature.³² The preparations were therefore carried out at a very low concentration of alkali. In accordance with the measured constants k_H , only 5 to 10 per cent. of the amino alcohol $\text{HO} \cdot \text{CH}_2 \cdot (\text{CH}_2)_n \text{NH}_2$ was to be expected as a by-product. The preparative tests, however, in the case of the 17-ring gave 15 to 20 per cent., in the 15- and 14-rings, 20 to 40 per cent., and in the 12-ring 60 to 70 per cent. oxamine as "by-product." These deviations from the calculated yields are far beyond the limits of the experimental error of the method. A part of the oxamine must be formed not by hydrolysis but by a side reaction of the first order. This

³² Hinshelwood and Grant, *J. Chem. Soc.*, 1933, 258.

type of reaction mechanism has recently been recognised for tertiary halogen alkyls, but on the other hand not for primary linked halogens.³³ For the halogenated amines the very unexpected course of the reaction becomes clear if the influence of the amino group on the ionisation process is taken into account:



The oxamine is formed as a result of the steric hindrance which is caused both by molecular structure and the hydration of the amino group. Since the oxamine is probably essentially less reactive than the ring formed, it polymerises to a lesser extent. Accordingly by the determination of yields the actual ratios are represented less favourably.

Nevertheless it cannot be doubted that the amino alcohol occurs as a result of reactions of the first order. The side reaction of course makes any conclusions from the temperature function more difficult to draw. It was, however, shown in the previous part how closely related the capillary activity of the solvent and the reaction velocity are for the 12-ring. If therefore instead of the ring, oxyamine is formed, the qualitative conclusions are not affected. The primary process of the thermal decomposition is, however, connected with the formation of a ring position.

Ring Closure and Polymerisation.

The question now arises, when can polymerisation take place at all? For the limiting concentration c , in which ring formation is the main reaction, the following equation holds approximately

$$c \cong 0.1 \times \frac{k_1}{k_2} \quad (1)$$

If $E_1 = E_2$, then in (1) $c = 0.1 \times \frac{Z_1}{Z_2}$. If the values for Z are those demanded by the theory then

$$c \cong 0.1 \times \frac{10^{13}}{10^{11}} = 0.1 \times 10^2 = 10 \quad (2)$$

The meaning of (2) is that polymerisation can only take place in imaginary 10 molar concentration. In other words, the ring formation reaction is favoured even in systems of very high concentration. This results from the fact that for monomolecular reactions the velocity depends on atomic vibrations but bimolecular reactions on the much slower movements of molecules. Thus 5- and 6-membered-ring systems are formed in good yields in concentrated solution. On the other hand, the formation of 3- and 7-membered-rings in water takes place with an activation energy which is essentially greater than in bimolecular reactions. Accordingly the limiting concentration c becomes dependent on temperature. The

³³ Hughes and Ingold, *J. Chem. Soc.*, 1935, 244. Hughes, *ibid.*, 255.

3-ring has such a favourable Z value (Fig. 3) that at 37° it is formed even in 0.2 molar solution. The Z value of the 7-ring is also favourable, but is already 50 times smaller and this suffices to reduce the limiting concentration to 0.005 mol./litre, somewhat higher concentrations can be used for the synthesis of the 7-ring in aqueous alcohol. The velocity of formation of the 17-ring in this solvent is only 20 times smaller (Table 8) and the limiting concentration is therefore of the same order of magnitude. Thus the speeds of reaction and limiting concentrations go through a minimum between the 7- and the 17-ring.

TABLE IX. —FORMATION OF THE 14-RING AT 73.35°C

Solvent.	k_1 .	k_2 .	c for k_1 .	c for k_2 .
30 per cent. Isopropyl .	0.0007	0.015	0.005	0.0025
Toluene	0.00000009	0.004	0.00002	?

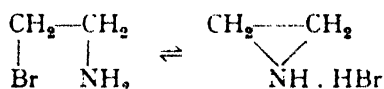
The circumstances in capillary active solvents are quite different. Whilst at 73° the speed of formation of the 7-ring in toluene is 80 times smaller than in 30 per cent. alcohol, it falls with the 14-ring to 800 times less. Since the bimolecular reactions in both solvents proceed with similar velocities (although with different temperature coefficients), for the synthesis of the 14-ring in toluene extreme dilution must be employed. Independently of the facts mentioned above, Table IX. shows clearly that *there is a specific relationship between solvent and reaction velocity*. The synthesis of the 14-ring in toluene proceeds at 73° to the extent of 99 per cent. in ten years, and at 128° in one year. Now we have at our disposal no method of separating the starting material from the final product, therefore it is impossible to prove that the ring is formed under the conditions given in Table IX. But for our conclusions the only important fact is the very small velocity of the reaction (independent of concentration), which causes the measurable changes in the order of magnitude of the limiting concentration. If instead of the ring, an isomeric compound is formed or if the ring is subsequently resinified, it does not in the slightest alter the fact that the velocity of the monomeric reaction is influenced 200 times more by the solvent than is the polymerisation reaction. On account of the exponential form of the temperature function the differences in velocity between iodine and bromine derivatives at high temperatures are small, being in the ratio of about 8:1. Consequently, the ring closures in xylene with the iodo amines proceed also too slowly to afford any proof of preparation.

In addition to polymerisation and the monomolecular reaction even reaction with the solvent can disturb the ring formation. In absolute alcohol, for example, the speed of etherification is of a similar order of magnitude to the speed of ring closure. Nitrobenzene was an exceptionally suitable solvent, except that it contained an active impurity (nitrophenol?). By working in very dilute solution an impurity in the solvent amounting to one millimole per litre is sufficient to disturb the speed of the ring closure. On the other hand the formation of the 6-ring in the same solvent proceeds so quickly and at so low a temperature that the impurities are absolutely inactive. On the same grounds the subsequent resinification of the large imines plays an appreciable rôle. If Ziegler's

method of dilution and reactions of long duration are anomalous in the practice of organic chemistry, the use of these methods resulted in entirely unexpected sources of error.

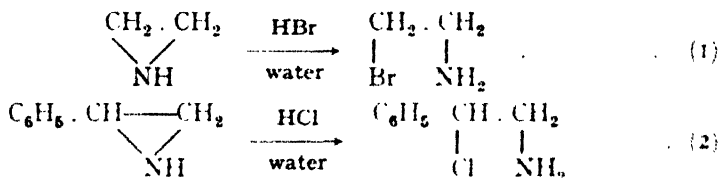
Strained Ring Systems.

Whilst the normal and higher membered rings which have been already referred to are stable to the halogen acids in dilute solution, the 3- and 4-membered rings imines are converted to the halogenated amines. The corresponding ring closure reactions, however, proceed to completion in alkaline solution, where the concentration of hydrogen ion remains small. In place of the equilibrium therefore, we have in alkaline solution a stationary condition. If on the other hand we have bromoethylamine in benzene, the following equilibrium is set up:



But instead of being as simple as this, very complicated processes take place. One sees from previous measurements that the equilibrium lies chiefly on the side of the bromoethylamine, which, however, is slowly removed from the equilibrium system by a slow primary polymerisation. This is very probably what occurs.

The breakdown of the ring systems is very strongly exothermic



In aqueous solution one finds in reaction (1) 5 K-Cal., and in (2) 10 K-Cal. less activation energy than is demanded by the ring closure reaction. Styroilimine is rearranged instantaneously in toluene solution even at -50° by HCl gas, so that this reaction requires only a very small energy of activation.

The formation of strained rings is thus, in contradiction to all other ring closures above, dependent on the p_H of the reaction mixture, so that it is not remarkable that the influence of alcohol on the reaction velocity in aqueous alcohol is large. This is in opposition to the Langmuir theory. In the 3- and 4-membered carbon chains there can be no difference in energy between the chain position and the ring position exceeding kT . But it depends here more on the spatial packing of the molecular compound which results. This compound, once formed in a capillary inactive solvent has probably a greater stability than in organic solvents.

For the preparation of strained rings an additional energy of activation is necessary (Fig. 4). The differences are, however, less than would be expected on the ground of the energy content (heat of combustion of cyclo-butane and cyclo-propane), and the small stability of the ring systems. The reaction is made less difficult by the halogen group in the β or γ position to the amino group.

As already explained, the large *a priori* probability of the formation of the 3-ring depends on the resonant action of the three atomic groups,

and also perhaps on the favourable spatial packing in water. It is astonishing that the *a priori* probability is at a minimum with the 4-ring, but this is probably due to the smaller resonance, higher mobility of the chain and deviation of the valencies. Perhaps, however, something else is decisive. The researches on the Raman spectra³⁴ of various butane derivatives shows that of the two possible forms the "zig-zag" form occurs much oftener than the "Wanne" form. Since it is this latter which is converted into the ring, it is the limitation of the free rotation of the chain determines the velocity of the reaction.

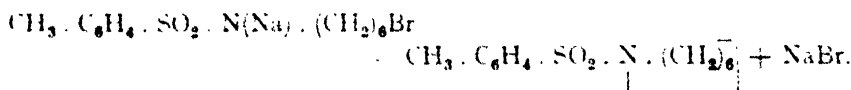
Comparisons with Other Ring Closure Reactions.

Bennett³⁵ and co-workers investigated a similar ionogenic reaction $R \cdot S \cdot (CH_2)_n Cl \rightarrow (R \cdot S \cdot (CH_2)_n)^+ Cl^-$, and Table X. shows how closely related both ring closures are.

TABLE X.

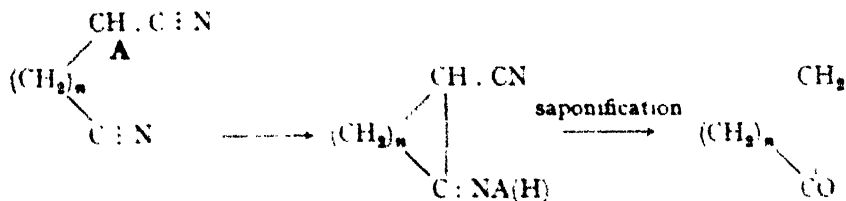
Reaction.	Solvent.	Ring	E.	H
$Cl-(CH_2)_n-S-C_6H_5$ $\rightarrow [C_6H_5-S-(CH_2)_n]^+ Cl^-$	50 per cent. Acetone	5 6	23.4 23.9	11.0 10.0
$Cl-(CH_2)_n-NH_2$ $\rightarrow (CH_2)_n-NH \cdot HCl$	Water	5 6	19.4 20.0	12.2 11.4
	30 per cent. Isopropyl alcohol	6	19.8	10.1

The following reaction was further developed by Ziegler³⁶ to the preparation of an imine derivative:



Preparative experiments have already shown that the reaction requires a large energy of activation. The synthesis of the 7-ring was accomplished as with the bromamines, at a dilution of the order of magnitude 0.01 mol./litre.

Ziegler's synthesis of the ketoimides is of an essentially different character; only the ring closure phase is given here:



A is alkali metal.

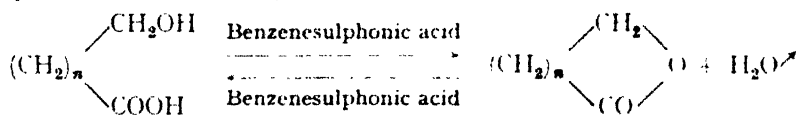
³⁴ Kohlrausch, *loc. cit.*

³⁵ Bennett, Heathcote, Mosses, *J.C.S.*, 1929, 2507.

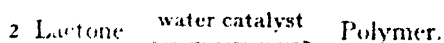
³⁶ Ziegler and Orth, *Ber.* 1933, 66, 1867.

The corresponding bimolecular reaction has between 25° and 36° a perceptible temperature coefficient. The energy of activation therefore must be at least 10 K-Cal. For the preparation of the 17-ring in boiling ether, a half-change period of the order of seconds or minutes was necessary, and the corresponding half-change period for the preparation of the 17-ring from the bromamine under the same conditions would be 10⁵ hours. This extreme difference depends not only on a greater activation energy for imine preparation, but also on the more favourable steric factors in the ketimide reaction. Whilst the ionogenic reaction in organic solvents proceeds slowly, this is obviously not the case in the ketimide synthesis. One can therefore expect that the bimolecular ketimide reaction proceeds with the velocity given by the collision theory. The ketimide is subsequently saponified to the ketone. Since the reaction products obtained here are unreactive, it is only by estimation of yields that conclusions may be drawn.³⁷

The large field of reversible ring closure reactions opened up by the method of depolymerisation developed by Carothers.³⁸ According to Carothers³⁹ the classical ketone synthesis of Ruzicka from the thorium salts of the dicarboxylic acids is due in part to a depolymerisation process. According to Langmuir long-chain molecules assume in the vapour phase the spherical or ring form, and this circumstance would contribute essentially to the success of such reactions. Ziegler⁴⁰ had neglected the application of the dilution principle to reversible reactions. It is easy to understand how in the dilute systems reversible reactions would be accompanied by side and secondary reactions. These circumstances accidentally prove to be very important in the preparation of many-membered lactones.⁴¹ The synthesis of these important perfumes was accomplished by Ziegler's⁴¹ method. In dilute benzene solution, the equilibrium is continually disturbed



by distilling off the water formed. Kinetically, the system is undefined since the process which defines the reaction velocity cannot be isolated, and conclusions drawn from yields or combinations of yields and kinetic measurements are also difficult to explain. Polymerisation by "Re-esterification" may occur thus:



Generally, one would not turn to the discussion of molecular statistics for catalytic reactions. In the first place a three-body collision with the catalyst is necessary and the shape of the molecule is then undeterminate. Esterification in moist organic solvents appears to be bound up with the fulfilment of an acidity condition which corresponds to p_H in aqueous solutions. We have at our disposal, then, only two types of reaction which will allow us to attempt to solve the polymerisation problem statistically: ionogenic reactions and the ketimide synthesis.

³⁷ K. Ziegler and R. Aurnhammer, *Ann.*, 1934, **513**, 43.

³⁸ *J. Am. Chem. Soc.*, 1929-35, last part, 1935, 929.

³⁹ Carothers and Hill, *J. Am. Chem. Soc.*, 1933, **5043**.

⁴⁰ *Ann.*, 1933, **504**, 94.

⁴¹ M. Stoll and A. Rouvé, *Helv.*, 1934, **17**, 1283.

During the last ten years there has been no lack of attempts to explain thermodynamically the "catalytic" influence of solvents on reaction velocity. Above all, the Van't Hoff-Dimroth theory should be remembered. According to these workers there should be a relationship between solubility, chemical equilibrium and reaction velocity. For ionogenic reactions, therefore, this explanation is insufficient as the dielectric constant of the medium is important. In inter- and intramolecular reactions, however, it appears that, in addition to the dielectric

constant, the spatial packing of the complex $R \cdot \overset{\boxed{\begin{smallmatrix} H_2N & Br \\ \text{solvent} \end{smallmatrix}}}{CH_2} \cdot R$ de-

termines the velocity. The ideas are similar to the old Van't Hoff theory, except that instead of the macroscopic equilibrium, the microscopic intermediary is considered. As long as we do not succeed in realising every typical chemical force which solubility can exert there is little hope of success in finding a quantitative relation between reaction velocity and solubility.

In the special case of the ring closure reactions we have moreover the complicated reaction mechanisms, simple relationships between capillary activity of solvent, shape of molecules, and speed of reaction.

I should like to take this opportunity of thanking Professor H. Freundlich for his warm interest in this investigation and Professor L. Ruzicka for the hospitality of his laboratory. My special thanks are due to the co-workers of Professor Ruzicka for their frequent and friendly advice which has so facilitated the execution of this work. I thank Mr. J. D. Rose for translating the manuscript.

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GENERAL DISCUSSION.

Professor R. Signer (Bern) said. In order to determine the form of fibre molecules in solution there are nowadays viscosity measurements, the determination of double refraction of flow and other methods available. The kinetic measurements of Salomon provide a criterion of the most probable form of the molecule of terminally halogenated amines. These molecules have two terminal groups with strong dipole moments, which will influence the distribution of the molecular form in solution. With regard to the first-named methods, one is led to ask whether from his kinetic measurements Salomon is in a position to say something as to the most probable form of the normal hydrocarbon molecule in organic solvents such as benzene, carbon, tetrachloride, etc.

Mr. W. F. K. Wynne Jones (Reading) said. According to the results presented in Table I., ring-closure reactions involving halogen alkylamines proceed at a normal rate in water, but at a rate which is about 10^4 times too slow in non-aqueous solvents. The theory of the activated complex predicts a normal rate wherever the activated state closely resembles the original state of the reacting molecules. For reactions of the type considered here, the theory therefore indicates that in water the reacting molecules are strongly polar and curled up in a ring form, since it is most probable that in the activated state ring formation is practically complete and the hydrogen and halide ions are in the act of leaving the complex.

In non-aqueous solvents the difference between the activated and normal states is evidently great, and this suggests that the normal state is much less polar than in water; such a change in polarity is well known in the amino-acids. Of course, any interpretation of the data in terms of a specific mechanism is dependent not only upon the reliability of the data, but also upon the assumption that the observed reaction behaves in a simple manner kinetically, but with these reservations the theory of the activated complex enables us to draw conclusions from rate measurements.

Dr. E. A. Moelwyn-Hughes (*Cambridge*) said: As Dr. Salomon has observed, there is a striking parallelism between the kinetics of the formation of piperidine hydrochloride and those of the formation of tetraethyl ammonium chloride in their response to different solvents (Table VI.). It therefore seems that the adoption, at least provisionally, of the Wigner and Polanyi figure of 10^{13} seconds⁻¹, or of the exact Raman frequency of the breaking bond, enables us to classify unimolecular behaviour in roughly the same way as the adoption of the gas-kinetic figure of 2.8×10^{11} seconds⁻¹ (gram-moles per litre)⁻¹ enables us to classify bimolecular behaviour. The parallelism revealed in the table is, however, quite independent of the value of Z_{uni} , or of Z_{bi} , which we accept as a kind of standard, and suggests that, of the various factors which are included comprehensively in the term P , at least one important factor is common to both sets of experiments. Another factor of possible significance for these reactions has been recently discussed.⁴²

With regard to Professor Ziegler's work on the union of two triphenylmethyl radicals, I do not think it is fair, until we have data for the reaction in the gaseous phase, to conclude that this reaction is slowed down by the solvent.

I have been fascinated by Dr. Salomon's ingenious method of calculating the statistical distribution of the various geometric forms of chain-like compounds in solution with the surface energies involved, and by his suggestion that such a distribution may contribute yet another factor to the complicated term P . As far as the reactions discussed here are concerned, it is difficult to gauge the amount of truth contained in the suggestion; but the method of attack is a novel and interesting one, and should yield further results of great value. If, in the present case, the mechanism is a relevant one, it appears to me that the form of the velocity constant concentration curve should throw some light on the problem. Provided

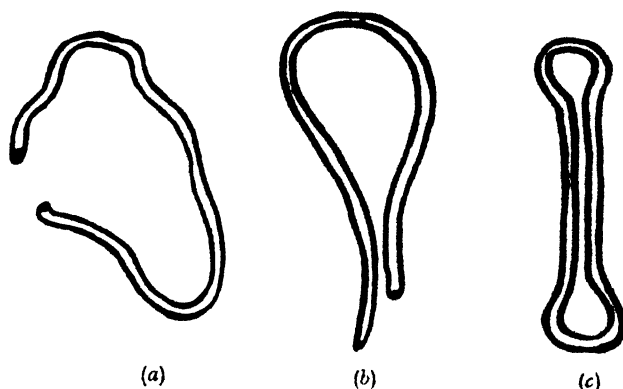


FIG. 1.

one geometric configuration were chemically more reactive than another, the form of the curve ought to be very sensitive to the magnitude of interfacial energy, λ . I should therefore like to ask Dr. Salomon what is the experimental range in which it is true to say

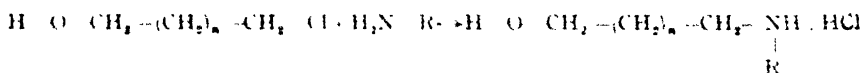
that "ring closure is independent of concentration?"

Professor H. Mark (*Wien*) said: The measurements of Dr. Salomon seem to show that in the case also of ring formation in solution, an effect takes place analogous with that in the case of polymerisation and association

⁴² Moelwyn-Hughes and Sherman, *Trans. Chem. Soc.*, in press, 1935.

of large molecules. The steric factors are not at all of the size which one would expect and may be compensated by another, as yet unknown, effect. One could think that, in some analogy to Volmer's ideas on crystal growth, and to the discussion which took place after my paper, the ends of a long chain do not diffuse in space at random until they approach one another, as shown in Fig. 1a, but that they are brought in contact by the internal van der Waals' forces, which bend the long molecules (Fig. 1b). The latter form of the molecule would have some analogy with the fact that large rings are built up of parallel chains, as shown in Fig. 1c.

Dr. G. Salomon (Zurich), in reply, said: I agree perfectly with Mr. Wynne-Jones. The change of the rate of reaction in various solvents must be very closely connected with the properties and the life-time of the preformed molecular compound. For the first time we observe a reaction with the "normal" rate in water and a "slow" rate in organic solvents. According to Eyring we may assume that the mechanism of reaction is connected with a restriction condition, when the rate of reaction should be slow. This effect may be inhibited by a longer lifetime of the unactivated complex. It is very probable that, having regard to the strong dipole forces in water, the intramolecular compound formed is stable and the regeneration of the open chain requires a small activation energy. Another argument for this opinion results further from this investigation. In addition to ring formation a new kind of monomolecular hydrolysis appears as a side reaction. This can only be understood if the hydrated sheaths are very strongly bound to the complex. Nevertheless the change of electrostatic forces in this "ionogenic" reaction cannot be the sole reason of the slow rate in organic solvents. The recombination of triphenyl methyl radicals to hexaphenyl ethane belongs also to this type. I outlined in this paper that there may be a connection between the spatial packing of the complex and the life period. Polanyi and Evans⁴² have recently drawn very similar conclusions, using the transition state method. It is difficult, however, to understand that two so different reactions as radical association and "ionogenic" reaction are restricted for the same reason. It may be possible that the same retarding effect follows from two very different causes. I believe that the kinetic test of a normal bimolecular amino condensation, for example,



will show that these "slow" reactions also become "normal" in water as solvent.

With Dr. Moelwyn-Hughes I believe it is right to be on the look out not only for "slow" but also for too fast reactions. But the hydrolysis he mentions in the discussion of Freudenberg's paper (page 75) is a much more complicated case than the one we are dealing with. As there are a series of different reactions of this type the temperature independent factor of which agrees well with Polanyi and Wigner's theory, there is no reason to neglect this idea as starting-point. It may nevertheless happen that by the indication of certain inner degrees of freedom the order of the Z-value increases and there may also be a small difference in the Z-value of the chloro-, bromo- and iodo-amines of the same chain according to the very different atomic weight of the halogen atoms.

Moelwyn-Hughes questions whether the geometrical equilibrium

Ring position \rightleftharpoons chain position

is not influenced by the concentration of the starting material. This certainly is right in concentrated solutions but not in dilution of 0.2-0.00002 mol./l. which are used for the kinetic experiments. Since large amounts

⁴² *Trans. Faraday Soc.*, 1935, **31**, 875.

of solute change the character of the solvent, the interpretation of experiments in high concentrations is ambiguous.

Professor Katz' gave some interesting results though they are not directly connected with our problem. Even the knowledge of the shape of molecules in a pure liquid does not permit us to draw conclusions as to the shape of the same molecule dissolved in another liquid.

The problems discussed by Professor Signer are connected with the question: which is the most probable form of a chain molecule. The kinetic results give data only as to the relative and absolute probability of one shape of the molecule, namely the closed form. Thus, it is possible to say that even the five-membered chain is about 10-30 times more seldom formed closed in water than would be expected on purely statistical grounds. We are sure, moreover, that a 17-membered chain in organic solvents is about 10^6 times more seldom closed than is the 5-membered chain. If there is, however, a certain internal movement it seems to me, according to Kuhn's and Mark's calculations, impossible that the chain is really straight.

THE KINETICS OF POLYMERISATION REACTIONS.

By C. E. H. BAWN.

Received 4th September, 1935.

It has long been recognised that the formation of a polymer of high molecular weight is a composite process, determined by a set of consecutive reactions. Some recent studies indicate that this process occurs via the successive addition of simple molecules to the growing complex. In these cases the total reaction process probably comprises a set of simple bimolecular association reactions between complex molecules. It is with this type of process that this paper is concerned.

The velocity constant of a bimolecular association reaction may be represented in the form

$$k = pZc \frac{E}{RT} \quad (1)$$

where Z is the total number of collisions between reacting molecules and p is a factor which takes into account the fact that not all collisions with the required energy lead to reaction. This factor is of especial interest since it broadly divides bimolecular reactions into two classes, (1) in which the factor p approaches the value of unity, and (2) in which p has a small value of the order of 10^{-4} to 10^{-8} . It has been pointed out by Hinshelwood and Grant,¹ that reactions in which one of the reacting molecules is an ion belong to the first class. The same is also true for bimolecular reactions of atoms. In the second group are included certain bimolecular reactions between large molecules ("slow reactions"), for example, processes in which tertiary nitrogen molecules form quaternary compounds with organic halides,² the recombination of free radicals³ and polymerisation,⁴ and hydrogenation reactions.⁵ Generally it may be stated that association reactions involving molecules having a large number of degrees of freedom have small steric factors.

¹ Grant and Hinshelwood, *J. Chem. Soc.*, 1933, 258.

² Moelwyn-Hughes, *Kinetics of Reactions in Solution*, Oxford 1933.

³ Zeigler, *Ann.*, 1929, 473, 163; 1933, 504, 124, 145.

⁴ Pease, *J. Am. Chem. Soc.*, 1930, 52, 1138; 53, 613.

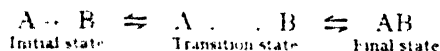
⁵ *Ibid.*, 1932, 54, 1876.

It is obvious therefore that this factor will play an important part in any kinetic considerations of a composite polymerisation process. It has been shown in a previous paper,⁶ that the application of the transition state method,⁷ for the calculation of reaction velocities, to association reactions leads to a simple interpretation of the steric factor. It is only necessary, therefore, to give a short account of these calculations. According to the method of Eyring and Evans and Polanyi⁷ the reaction velocity may be represented by

$$\text{reaction velocity} = \frac{1}{2} P v$$

where P is the probability of the transition state and v is the average velocity of the representative point at the top of the barrier, along the reaction co-ordinate L . This may be shown to be equal to $\frac{1}{2} K \cdot v$ where K is the equilibrium constant between the initial and the transition state. Now both K and v may be calculated by the method of statistical mechanics together with a knowledge of the potential energy surface which represents the course of the reaction.

Thus in the general case of a reaction



where A and B are complex molecules K may be calculated from the partition functions of the molecules

$$K = \frac{f_{A \cdots B}}{f_A f_B} e^{-E_0/kT},$$

where E is the difference in energy between the initial and the transition state. The average velocity associated with the passage of the system across the transition state is $\frac{kT}{(2\pi m^* kT)^{1/2}}$ where m^* is the reduced mass of the transition complex, so that the reaction velocity constant k_1 is equal to

$$k_1 = \frac{f_{A \cdots B}}{f_A f_B} \cdot \frac{kT}{2\pi m^* kT} e^{-E_0/kT} \quad (2)$$

By comparison with equation (1) it is seen that the first term in the above expression now replaces * the factor pZ . If this expression could be separated in the correct way it would be possible to obtain the absolute values of p and Z . However, this requires some assumptions as to the detailed mechanism of the reaction, and for the present the approximate magnitude of p may be obtained by comparison of the calculated factor with Z as obtained by the ordinary kinetic theory method. Before we give the results of these calculations, further considerations will show clearly the origin of the steric factor. If the expression analogous to (2) is written down for a similar reaction between atoms, a comparison of the probability factor for the transition state in these two cases shows immediately that for complex molecules the probability is very much decreased. This decreased probability appears in the kinetic expression for the reaction of the complex molecules as a steric factor.

* *Trans. Faraday Soc.*, 1935, **31**, 1536.

⁷ Eyring, *J. Chem. Physics*, 1935, **3**, 107. Evans and Polanyi, *Trans. Faraday Soc.*, 1935, **31**, 875.

* This is not exact since a small term will have to be included to allow for the fact that E_0 in equation (2) and E in (1) are defined differently (see ref. 7).

It may now be seen, by tracing the change in the degrees of freedom which occur, how the reduced probability in the reactions of complex molecules arises. In the association reaction of atoms two degrees of translation in the initial state pass over to two degrees of rotation in the transition state. This roughly corresponds to the collision diameter in the kinetic theory picture. In the case of the reaction between complex molecules, *e.g.*, the association of two radicals, two degrees of freedom of translation and three of rotation go to five degrees of vibration in the transition state. The steric factor can now be correlated with the change from rotational to vibrational degrees of freedom.

Calculation of the Steric Factor for some Association Reactions.

The equilibrium constant of an association reaction may be written in the form

$$K = \frac{k_{\text{uni}}}{k_{\text{bi}}} \quad (3)$$

where k_{uni} and k_{bi} are the velocity constants for the forward and reverse reactions respectively. If the unimolecular part of the reaction involves no steric factor, then the full magnitude of the steric factor of the bimolecular reaction will make its appearance in the equilibrium constant. The former assumption will be generally true since the configuration of the transition state of the unimolecular reaction will be very similar to that of the initial state⁸—it will probably differ only in one co-ordinate along which decomposition is occurring.

The following table gives the steric factors of some simple reactions calculated by use of (3). The equilibrium constant was determined from the partition functions of the molecules.⁹ The value of p was obtained by comparing k_{bi} calculated from (3) (it being assumed that

TABLE I.

Reaction.	Temperature °C.	K (atm.)	p .
$\text{CH}_3 + \text{I} \rightleftharpoons \text{CH}_3\text{I}$	600	1.9×10^{-14}	1
$\text{CH}_3 + \text{CH}_3 \rightleftharpoons \text{C}_2\text{H}_6$	1500	7.43×10^{-8}	$10^{-4} - 10^{-5}$
$\text{CH}_3 + \text{COCH}_3 \rightleftharpoons \text{CH}_3\text{COCH}_3$	1500	2.75×10^{-11}	8×10^{-6}
$\text{CH}_3 + \text{C}_2\text{H}_5 \rightleftharpoons \text{C}_3\text{H}_8$	800	9.0×10^{-9}	$10^{-4} - 10^{-5}$
Log K_p (atm.).			
$\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$	—	$-\frac{13600}{2.3 RT} + 9.0$	2×10^{-6}
$\text{C}_2\text{H}_6 \rightleftharpoons \text{C}_2\text{H}_4 + \text{H}_2$ ¹⁰	—	$-\frac{31244}{2.3 RT} + 6.31$	1×10^{-2}
$\text{C}_2\text{H}_4 + \text{H}_2\text{O} \rightleftharpoons \text{C}_2\text{H}_5\text{OH}$ ¹¹	—	$-\frac{9600}{2.3 RT} - 6.20$	1.4×10^{-4}

⁸ This assumption was employed by Polanyi and Wigner (*Z. physik. Chem., Haber Band*, 1928, 439) in their derivation of the well-known relationship $k_{\text{uni}} = \nu e^{-E/RT}$.

⁹ Cf. ref. 6 for details of these calculations.

¹⁰ Pease, *J. Amer. Chem. Soc.*, 1932, **54**, 1876.

¹¹ Stanley, Yould and Dymock, *J. Soc. Chem. Ind.*, T., 1934, **53**, 206.

$k_{\text{uni}} = 10^{13} e^{-E/RT}$ where no experimental determination was available) with the corresponding value of the collision theory. The last three results in Table I. were calculated from the experimentally determined temperature dependence of the equilibrium constant. It can be seen from these results that association reactions between molecules involving a large number of degrees of freedom have small steric factors, whereas with reactions involving atoms the steric factor tends to unity. These conclusions are strongly supported by experimental measurements of the rates of such reactions. (Table II.)

TABLE II.

Reaction.	$B.$ $(\log k = B$ $- E/2.3 RT)$	$E.$	p (600° C.).
$H_2 + C_2H_4 \rightarrow C_2H_6$ ¹⁰	—	35,700	4.5×10^{-3}
$2C_2H_4 \rightarrow C_4H_8$ ¹¹	10.85	38,400 (40,300)	4×10^{-3} (3×10^{-3})
$2CH_2 = CH - CH_2 \rightarrow C_6H_{12}$ ¹²	10.2	38,000	1×10^{-3}
$2CH_2 = CH - CH_2 \cdot CH_3 \rightarrow C_6H_{14}$ ¹²	10.0	38,000	5×10^{-4}
Amylene ¹²	9.8	38,000	4×10^{-4}
$2 \begin{smallmatrix} CH_3 \\ \\ CH_2 \end{smallmatrix} \cdot C = CH_2 \rightarrow C_8H_{16}$ ¹²	12.3	43,000	1×10^{-1}
$2CH_2 = CH - CH = CH_2 \rightarrow C_6H_{10}$ ¹³	—	25,300	1×10^{-4}
$2CH_3 - C \begin{smallmatrix} \diagup CH_3 \\ \diagdown CH \end{smallmatrix} - CH_3 \rightarrow C_{10}H_{18}$ ¹⁴	—	28,900	1.0×10^{-2}

Before extending the application of these ideas to complex polymerisations the theoretical conclusions may be summarised as follows:

(1) On account of the decreased probability of the transition state bimolecular association reactions between complex molecules will have a much smaller steric factor than the corresponding reaction in which one or both of the reaction partners is an atom. In the latter case the value of the steric factor tends to unity.

(2) The steric factor will for a series of similar reactions decrease as the number of degrees of freedom of the associating molecules increase.

(3) In comparing dissimilar reactions account must also be taken of the configuration of the transition state. The transition state may be considered as a potential hollow of $3N - 7$ dimensions and the volume of phase space corresponding to it will be determined by the restriction of position placed upon the molecules in the transition state. Since this phase volume is proportional to the probability of the state any increased restriction of position will decrease the probability and thus the steric factor. Thus the third conclusion may be stated—the greater the restriction of position of the reacting molecules in the transition state the smaller the steric factor.

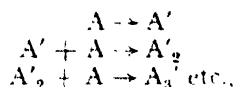
¹² Krautz, Nemtsov, and Soskina, *Compt. rend. Acad. Sci. U.R.S.S.* Figures in brackets, Pease, *J. Amer. Chem. Soc.*, 1931, **53**, 613.

¹³ Vaughan, *ibid.*, 1932, **54**, 3863.

¹⁴ *Ibid.*, 1933, **55**, 4108.

Polymerisation as a Chain Reaction.

Polymerisation reactions are known to show many of the characteristics of chain reactions.¹⁵ The evolution of the polymeric molecule may be imagined to proceed by the successive addition of single or more complex molecules to the growing complex. As an example the following type of chain may be considered. The polymerising molecule A may be activated either thermally or photochemically and this activated molecule then combines with another molecule of A to give a dimer. It is further assumed that the dimer is produced in an activated condition, the activation being produced by the energy of reaction. This process continues until either the intermediate active polymer becomes deactivated or that it is incapable of adding more molecules for chemical reasons. The total process may be represented by the following scheme,*



it being assumed that the dimers, trimers, etc., do not react among themselves. Now from our previous considerations if A is a complex molecule each succeeding step in the reaction chain requires a smaller steric factor. That is, as the chain length increases, reaction becomes more difficult and will finally become immeasurably small. The length of the chain and hence the size of the polymeric molecule will therefore reach an apparently limiting value and this will be determined primarily by the magnitude of the steric factor.†

In drawing these conclusions it has been assumed that all unit reactions in the chain require no activation energy. If such reactions needed activation it might be suggested that this energy decreased at each stage in the reaction and that this annuls the effect of the decreasing steric factor. The fact that the reaction chain extends to any considerable length excluded this and, furthermore, experimental evidence indicates that the association of radicals which are probably intermediates¹⁶ in the chain needs no activation energy.

¹⁵ Semenoff, *Chemical Kinetics and Chain Reactions*, Oxford 1935, p. 444.

* A well known example of this type of process is the polymerisation styrene or vinyl acetate. Both of these reactions are known to proceed by a chain mechanism. The initial process is most probably the opening of a double bond,



the active molecule then adding another molecule of the monomer, the energy change being sufficient to give an excited dimer which may carry on the chain in the following way.



† There are several possible variations of the foregoing reaction scheme, for instance: the initial reaction $A + A \rightarrow A_2$ may give a dimer which does not participate in a reaction chain. The possible subsequent reaction of the dimer (say with another molecule of A) would need an activation energy and similarly for the reaction of higher polymers. In such cases the resulting polymeric mixture when all of A has disappeared would consist almost entirely of lower polymers, the concentration of the dimer being much greater than that of the trimer, the concentration of the trimer greater than that of the tetramer and so on.

¹⁶ Rice and Sickman (*J. Amer. Chem. Soc.*, 1935, **57**, 1384) have recently found that methyl radicals initiate the polymerisation of ethylene.

Further information can be obtained by a consideration of the reverse process, namely, the breakdown of a long chain, or large polymeric molecule. A molecule built up of n unit molecules of A may break in any one of the $n - 1$ bonds, the two limiting reactions being given by



Since the association reaction is more difficult for the larger molecule, then, if the unimolecular dissociation is assumed to require the same activation energy independent of the bond which breaks, the equilibrium constant of (1) will be shifted much further to the right than that of (2). Thus, if the equilibrium is established the products of the breakdown in the middle of the molecule will be more abundant than those corresponding to dissociation at the end of the chain. This is also in general agreement with many observations on the cracking of hydrocarbons.⁶ It is also well known that the stability of the hydrocarbon molecule decreases with increase in chain length, as is also true for large polymeric molecules. In other words k_{uni} actually increases with increasing chain length and, since k_{bi} decreases under the same conditions, it may be concluded that for any similar series of long chain molecules the equilibrium corresponding to the breaking of any given bond will be displaced more to the right the longer the length of the molecule.

Summary.

The steric factor of bimolecular association reactions has been discussed. The application of the transition state method for the calculation of reaction velocities leads to a simple interpretation of this factor in terms of the probability of the transition state. The steric factor of some polymerisation reactions has been evaluated. On the assumption of a chain mechanism of polymerisation it is shown that the chain length and thus, the size of the polymeric molecule, is determined by the magnitude of the steric factor.

In conclusion, the author wishes to thank Professor M. Polanyi for many helpful discussions.

*The University,
Manchester.*

GENERAL DISCUSSION.

Dr. H. Dostal (Wien) said. If the reaction constants of chain growth,

$$\begin{aligned} A'_1 &= A \cdot A'_1 \dots k \\ A'_2 &= A \cdot A'_2 \dots k_1 \\ &\vdots \\ A'_n &= A \cdot A'_{n+1} \dots k_n \end{aligned}$$

k_n depend on the degree of polymerisation (or chain length, which is the same) n , our method of calculating the amount of polymer at any time, and the distribution of the molecular weights in the polymer, cannot be applied immediately. With regard to the steric factor, the function k_n of n can, for instance, be given by

$$k_n = A\alpha^n.$$

We can, also, use a transformed measure of chain length m , which is not identical with the degree of polymerisation. m and n are regarded as continuous, and m defined by

$$\frac{dn}{dm} = k_n \quad (I)$$

especially

$$\frac{dn}{dm} = Ax^n \quad (1')$$

The velocity of chain-growth *relative to m* becomes uniform and the results communicated in our paper are applicable when, instead of *n*, *m* is used. The relation between *m* and *n* is given by (1), (1') or

$$m = \int \frac{dn}{k}, \quad (2)$$

especially

$$m = \int_0^{\infty} \frac{1}{A} \left(\frac{1}{x} \right)^n dx \quad (2')$$

so that the true degree of polymerisation n can be found easily from m in any case.

any case.
Professor E. K. Rideal (*Cambridge*) said: It is clear that polymeric growths regarded as chain reaction fall into at least three categories, those in which the chains grow after initiation at ever decreasing speed due to the operation of an increasing steric factor. The second class consist of reactions in which the chains grow by collision and an energy of activation is required for each addition of a new monomeric molecule, i.e., they consist essentially of a sequence of regular bimolecular reactions. The third class include those in which the chains grow after initiation without any perceptible variation in speed as the chains get longer. These reactions suggest the absence of or small steric factor and a constantly activated end, i.e., a free radical requiring a negligible energy of activation. The chains appear to grow remarkably fast and if they really grow faster than can be accounted for by a collision mechanism then it would appear better to regard their growth as examples of the growth of thread like crystals where surface diffusion plays such an important part in the supply of reagent

Professor H. Mark (H'ien) said: I desire to mention once again that long chains, rings and associations of big molecules in solution occur too quickly. One would expect, from theoretical considerations, that the rate of their formation should be much smaller. The experimental material, which as yet is not at all convincing, or even satisfying, leads to the estimate that these reactions are about 10^4 to 10^5 too rapid, if they are compared with our general knowledge of the kinetics of bimolecular gaseous reactions. Some, as yet unknown, factor seems to play an important rôle in these solutions, and to compensate the influence of the steric factor. In fact, we are able to show, in the case of non-catalysed polymerisation reactions, that they are much slower in the gaseous state, than in solution. This agrees with an investigation of Rice and Greenbaum, who found that the dimerisation of pentene proceeds much more rapidly in the liquid phase than in the gaseous.

We should surely try first to consider the energetics of the influence of the solvent, and we should expect that the heat of activation is lowered in the solution. The present experimental material does not exclude this possibility entirely, but the activation energy is already, in the gaseous state, especially in polymerisation reactions, so small, that a further decrease cannot influence the reaction very much. We conclude therefore, that the solvent may affect in a certain way the statistical frequency of the collisions between large molecules in the soluted state. It may be that a certain amount of "*Schwärmbildung*" cancels out the influence of

the steric factor. Whether we should, with E. Hückel, take into account the phase volume, or whether we must choose another possibility, cannot as yet be said with certainty. In any case, however, it seems that a further systematic study of the dissociation reactions of big molecules (independent of the solvent) seems to be mostly in demand.

Dr. E. A. Moelwyn-Hughes (*Cambridge*) said: The theory of Polanyi and Eyring is essentially an equilibrium theory. How far does Dr. Bawn consider it logical to apply this theory to a system involving a chain reaction, which only under highly specified conditions can be treated as a system at equilibrium? I should also much appreciate any comments which Dr. Bawn might feel disposed to make on some of the postulates underlying the theory of Eyring and Polanyi, particularly (1) the mutual independence of the various intermolecular motions which is implied in the evaluation of the corresponding partition functions, and (2) the force-free field postulated for the translatory motion in the co-ordinate of decomposition.

Mr. M. W. Perrin (*Northwich*) said: In connection with the "transition state" method of treating reaction kinetics, I should like to mention some preliminary results which have recently been obtained for the influence of hydrostatic pressure on the rate of polymerisation of linseed oil. Estimating this rate by the time taken to produce an oil of any given viscosity, it has been found that a pressure of 3000 kg./cm.² accelerates the reaction about ten times. At a temperature of 280° C., where the reaction is so slow at atmospheric pressure that a time of some days is necessary to reach a high viscosity, it has been found that the oil is polymerised to a hard gel in about one hour under a pressure of 12,000 kg./cm.²

Until more experimental data is available, it is not possible to make an exact numerical comparison with the theory put forward by Evans and Polanyi,¹⁸ but it appears that the pressure effect is of the order of magnitude predicted for a polymerisation reaction of the "slow" type with a steric factor much smaller than unity. It is hoped that further work, now in progress, will enable more definite conclusions to be drawn as to the mechanism of the pressure effect.

Mr. W. F. K. Wynne-Jones (*Reading*) said: The theory of the activated complex or transition state as developed by Eyring,¹⁹ and by Evans and Polanyi²⁰ leads, as shown by Bawn, to a decreased probability for the formation of complex molecules. It is, however, important to note that for reactions occurring in solution the association of solvent molecules with the activated complex or the reacting molecules may have a preponderating influence, as has already been shown for certain reactions.¹ The criticism raised by Moelwyn-Hughes refers to the exact calculation of the partition function for the activated complex, and does not reflect on the principle of the method, nor does it affect the general conclusions that may be drawn as to reaction mechanism. It has already been shown in several studies made by Eyring and his co-workers that abnormal rates of reaction in the gaseous state can be exactly treated by this method.

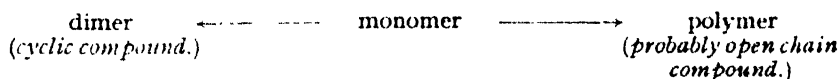
Professor Paul N. Kogerman (*Tartu*) said: In spite of the great importance of physico-chemical methods and mathematical analysis for the study of the phenomenon of polymerisation, especially for elucidation of the kinetics of the reaction, one should nevertheless not exclusively depend upon these methods but, from the organic chemist's point of view in the first instance, study the *mechanism* of the reactions of polymerisation, and determine the quantity and the structure of the products of polymerisation. In many cases it has been found that the process of polymerisation of unsaturated hydrocarbons, in particular conditions, *taken as whole*, is not a simple chain reaction; at least two processes take place simultaneously. For instance, in the case of polymerisation by heat of

¹⁸ *Trans. Faraday Soc.*, 1935, **31**, 875.

¹⁹ *J. Chem. Physics*, 1935, **3**, 402.

²⁰ *Trans. Faraday Soc.*, 1935, **31**, 875.

isoprene and methyl isoprene at temperatures above 150°C . the reaction proceeds according to the following scheme :—



At higher temperatures, *i.e.*, at 200°C ., the dimer begins to polymerise, and the product of polymerisation is, therefore, a mixture of compounds which do not belong to the same homologous series. The ratio of dimer to polymer in the case of methyl isoprene (at 150°) is 2 : 2 : 1.²¹

If we assume that the process of polymerisation (in analogous cases) is a chain reaction, and base our calculations on this assumption, it might easily happen that the conclusions arrived at have nothing to do with the facts of the case.

Dr. G. Salomon (Zurich) said: I would like to mention once more the great difficulties in understanding the mechanism of "slow" reactions. As is well known, several factors may influence the rate of reaction, so in many cases we have no means of deciding which of these has the mayor effect. There are two extremely different types of "slow" reactions: radical association and amino condensation.

For the first type the association itself is slow and there should be no solvent effect. On the other hand from my own experiments it seems very probable that amino condensation is a normal reaction, only retarded by organic solvents. It will be necessary to investigate the lifetime of the unactivated amino halogen alkyl complex in different solvents to decide the real cause of these abnormalities. If there is a connection between the solubility of the compound formed and the rate of reaction then the number of CH_2 -groups in the reacting molecules should also influence the rate. For example cyclo-hexadecamethylenimine hydrobromide is readily whereas piperidine hydrobromide is only slightly soluble in benzene.

It is moreover obvious that an intermediary change of valency in the nitrogen atom may also influence the reaction; but it does not seem possible to express this change in a more quantitative manner.

Dr. C. E. H. Bawn (Manchester) said, *in reply to Professor Mark*: It is to be expected, as pointed out by Evans and Polanyi,²² that the collision number in solution may be as large as 10^{12} (the corresponding value for gaseous reactions being 10^9 - 10^{10}). This increase, together with a decreased activation energy (which will be dependent on the solvent) may account for the increased reaction rates in solution, especially in simple cases such as the bimolecular polymerisation of ketene.²³

In reply to Dr. Mochelvy-Hughes: (a) The formation of high molecular weight polymers was considered as occurring by a series of consecutive bimolecular reactions. The transition state method was used to evaluate the steric factor of these (bimolecular) reactions and was not applied to the reaction as a whole. A knowledge of these separate bimolecular constants suffices to calculate the total rate and to allow of certain conclusion regarding the final chain reaction.

(b) It is assumed in evaluating the partition function for the transition state that the vibrations are harmonic. This is admittedly an approximation which seems to be good for normal molecules,²⁴ and leads directly to the conclusion that the intermolecular motions are independent of each other. If this condition does not apply then it is not possible to evaluate the partition function. By making this assumption it may be shown that

²¹ For particulars, see: P. N. Kogerman, *Additionsreaktionen und Polymerisation des 2, 3-Dimethylbutadiens*, Sitzungsber. d. Naturforscher-Gesellschaft bei der Universität Tartu, Band XLI, 1934.

²² *Trans. Faraday Soc.*, 1935, **31**, 875.

²³ Rice and Greenberg, *J.A.C.S.*, 1934, **56**, 2132.

²⁴ Cross and Van Vleck, *J. Chem. Physics*, 1933, **1**, 357.

unimolecular dissociations follow the rate-law $k = ve^{-E/RT}$ which we know is closely obeyed. This relationship was used in arriving at the results of Table I.

(c) The transition state is defined by a co-ordinate²⁵ which is tangential to the reaction path at the top of the potential barrier. It follows, therefore, that $\frac{dV}{dt} = 0$ at the transition state, and, thus the force will be zero.

²⁵ Eyring, *J. Chem. Physics.*, 1935, **3**, 107.

POLYMERISATION IN MONOLAYERS.

By GEOFFREY GEE.

Received 10th July, 1935.

Polymerisation in Monolayers.

The purpose of the present communication is to describe briefly an investigation of the polymerisation of drying-oils accompanying the process of "drying" when the material is spread as a unimolecular film on the surface of water or dilute acid.

No complete agreement has been reached as to the mechanism of the drying of oils, and in particular the role of oxygen remains a matter of discussion, but all workers are agreed that polymerisation plays an important part in producing the final varnish film. Probably the largest body of opinion now regards the drying process as consisting of an oxidation of the unsaturated linkages of the oil to peroxides, which subsequently polymerise.^{1, 2} It will be shown that a mechanism essentially similar to this gives a complete and self-consistent explanation of the experiments which are described below.

Experimental Methods.

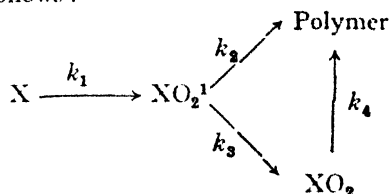
The material employed in the investigation was the maleic anhydride compound of β -elaeostearin described by Morrell.³ We are indebted both to Dr. Morrell and to the British Dyestuffs Corporation for specimens which gave similar results. Unimolecular films were spread from benzene on a trough of $N/100$ H_2SO_4 , and provision was made for the simultaneous measurement of surface pressure—by means of a Langmuir torsion balance, and phase boundary potential. The trough was completely enclosed in a thermostated box and the apparatus so arranged that all measurements and adjustments could be made from outside.

The characteristics of a freshly spread film were entirely in accord with those to be anticipated from the formula proposed for this material by Morrell but it was found that the films were unstable and rapidly underwent a spontaneous reaction, accompanied by changes in both the surface pressure and potential. It is clear that these changes may be employed as the basis of a study of the reaction kinetics, and it has been found most convenient to work at constant pressure, measuring the area and potential at suitable intervals.

¹ Elm, *Ind. Eng. Chem.*, 1931, **23**, 88.

² Morrell, *Ind. Chem.*, 1925, **1**, 68; *J. Oil. Col. Chem. Assoc.*, 1929, **12**, 183, 1930, **13**, 84; *J. Soc. Chem. Ind.*, 1931, **50**, 27 T.

The reaction is found to be far from simple, but can be represented schematically as follows:



Here X represents the initial unsaturated glyceride, which first oxidises (k_1) to a peroxide XO_2^1 , which is however unstable and may react in either of two ways:

- (a) by polymerisation (k_2), or
- (b) by isomerisation (k_3) to a more stable body XO_2 .

Finally, the latter may also polymerise (k_4).

The product which is obtained on oxidation thus depends on the experimental conditions: at high pressure $k_2 \gg k_3$ and the XO_2 stage is not observed; while at low pressure $k_3 \gg k_2$ and the XO_2 formed remains stable unless the pressure is raised. By suitable adjustment of the conditions of temperature and pressure, the polymerisation of the two oxidised forms can be studied separately, as described below.

Polymerisation of the Oxidised Oil.

The evidence that the final products obtained are polymeric in nature is derived in part from a consideration of the nature of the final film.

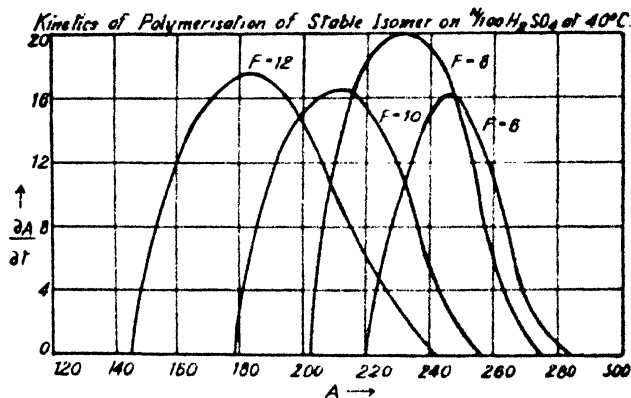


Fig. 1.

During the course of the reaction a fluid film of β -elaeostearin becomes converted into a continuous gel-like structure, while the maleic anhydride compound gives highly viscous products which break up on extension. It is suggested that the difference

between these two cases arises from the greater ease of cross-linking between the molecules in the former. Further evidence of the nature of the process is given by the effects of the various kinds of positive and negative catalyst which have been employed (see below).

The simpler polymerisation process to investigate experimentally is the one represented above by the constant k_4 . It will be clear from the foregoing that by carrying out the oxidation at a low pressure a film of pure XO_2 can be produced if time is allowed for the isomerisation to be complete (10 to 15 minutes at 40 to 30° C.). If such a film be now compressed to a high pressure, polymerisation occurs and can readily be followed. Fig. 1 represents some typical curves of dA/dt plotted as

a function of the area per molecule A , and it will be noted that these curves are approximately parabolic in shape, but that the maximum is somewhat displaced towards the commencement of the reaction.

The polymerisation of the unstable peroxide XO_2^1 can be approached in two ways. At low temperatures and high pressures $k_2 \gg k_1$, so that the whole process ($\text{X} \xrightarrow{k_1} \text{XO}_2^1 \xrightarrow{k_2} \text{polymer}$) is pseudo-unimolecular; but at high temperatures and lower pressures this is no longer the case; the two processes can then be observed to proceed successively. Some representative velocity curves are given in Fig. 2, in which a separation of the lower pressure curves into two portions, of which the second is roughly parabolic in shape, is to be observed.

This method of investigation is limited to those special cases in which the values of k_1 and k_2 are within certain fairly narrow limits: the method now to be described is more generally applicable. If a film is spread and allowed to oxidise completely at low pressure the product will consist of a mixture of the two oxidised forms, the proportions of which will change progressively with time. Such a film may now be compressed, when the predominant reaction will be the polymerisation of XO_2^1 (k_2), which can therefore be followed. It is found that the stable material (XO_2) present acts as an inhibitor at low temperatures, when it is evidently incapable of taking part in the polymerisation chain, but a correction can easily be applied by calculating the concentrations of XO_2 in a series of films which have been oxidised for various lengths of time, and extrapolating the polymerisation constants to zero concentration. It is found that $1/k$ is roughly a linear function of the XO_2 concentration (α) as would be anticipated from the well-known equation

$$k = \frac{k_0}{1 + \alpha\epsilon}.$$

Fig. 3 gives some velocity curves obtained in this way, and the same general shape is evidenced, but the displacement of the maximum towards the start of the reaction is now much more pronounced.

Reaction Kinetics.

In seeking an interpretation of the shape of the velocity curves two distinct methods of approach have been employed. The first of these

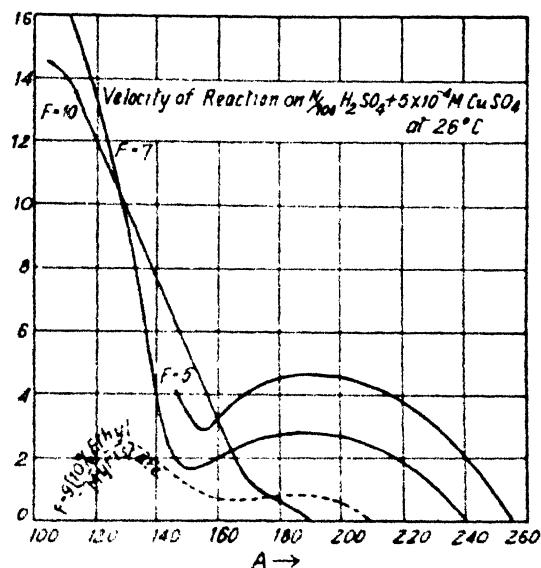


FIG. 2.

is based on the analysis given by Semenov³ of the induction period considered from the point of view of thermal gaseous chain reactions. The fraction ξ of the original material undergoing reaction in time τ , reckoned from the time of half reaction, is given by

$$\xi = \frac{1}{1 + e^{-\phi\tau}} \quad (1)$$

where ϕ is a function of temperature and pressure of the form

$$\phi = Bp^n e^{-\frac{K}{RT}} \quad (2)$$

For experiments with monolayers, in which A is the dependent variable we may put

$$\xi = \frac{A - A_0}{A_\infty - A_0} \quad (3)$$

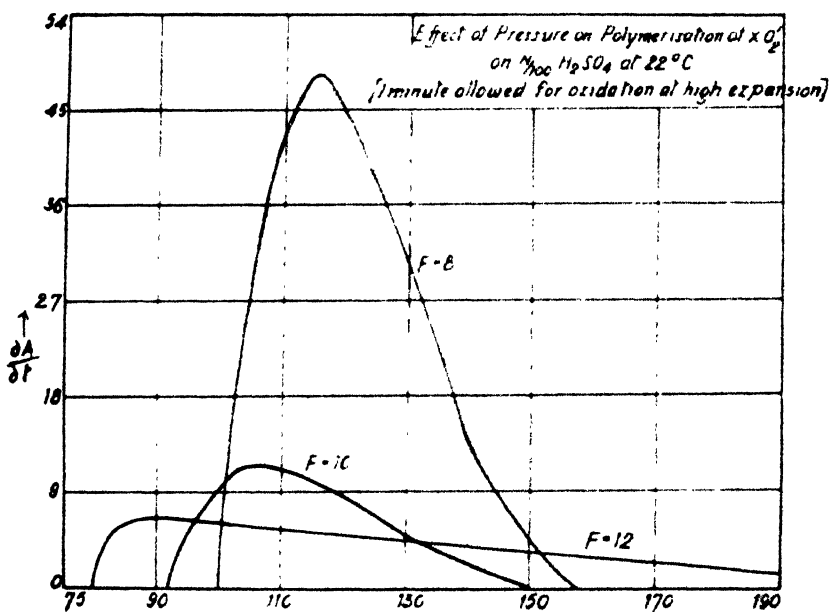


FIG. 3.

where A_0 and A_∞ are initial and final areas. It is then easily shown that

$$\frac{dA}{dt} = \frac{k_s}{A_\infty - A_0} (A_\infty - A)(A - A_0), \quad (4)$$

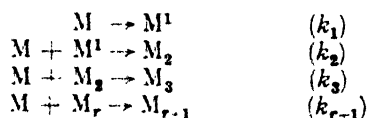
in which k_s is written for ϕ . The plot of dA/dt against A required by (4) is clearly parabolic, a form which is closely approached by many of the experimental curves.

For the cause of the observed divergencies from the parabola we must consider an attempt which has been made⁴ to analyse the kinetics of a polymerisation chain initiated by the slow primary activation of the monomer followed by the rapid reaction of the product with successive

³ Semenov, *Z. physik. Chem.*, 1931, **B 11**, 464; *Physik. Z. der Sowjet*, 1933, **4**, 906.

⁴ Gee and Rideal, *Trans. Faraday Soc.*, 1935, **31**, 969.

molecules of inactive monomer. If the mechanism is represented by the following equations it can be shown that the observed kinetics are derivable on the assumption that the chains are stopped only by an increasing steric factor.



The various constants may be expressed as functions of r in terms of a parameter K , a typical case which is considered being given by

$$k_{r+1} = K/r, \quad (5)$$

while k_1 is included in the general scheme by putting

$$k_1 = \alpha n_0 K \quad (6)$$

where n_0 is the original number of molecules present and α is a numerical constant. The analysis which has already been given (*loc. cit.*) derives the reaction velocity in terms of the total number of molecules N present at time t , and is not therefore directly applicable to the present case. We require also some relation between the size of a polymer molecule and the area it occupies on the surface. Four possible laws have been investigated, but since all lead to essentially similar results, it will be sufficient for the present purpose to illustrate the method by considering the simplest case, in which the area A_r of the r -mer is given by

$$A_r = A_0 + r \cdot \Delta A \quad (7)$$

where ΔA is a constant.

On this basis, it can be shown that the velocity equation takes the form

$$\frac{dA}{dt} = \frac{2\nu + 1}{\nu^2 \Delta A} K n_0 (A_0 + \nu \cdot \Delta A - A)(A - A_0) \quad (8)$$

where ν is the mean chain length of that portion of the material which has polymerised at time t .

Two extreme forms of curve are predicted:

(a) If ν be equated to ν_∞ , its value at the end of the reaction, equation (8) takes the same form as (4) by putting

$$\frac{(2\nu_\infty + 1)Kn_0}{\nu_\infty^2 \cdot \Delta A} = \frac{k_s}{(A_\infty - A_0)} \quad (9)$$

Thus for a reaction in which the chain length of the polymer does not change greatly during the reaction, an approximation to the parabolic form would be anticipated, and this should be realised in practise for short chain processes.

(b) If α is small it is easily shown that the reaction becomes pseudo-unimolecular, a form which we should therefore expect for long chain processes.

The observed forms of curves are thus readily explicable in terms of this kinetic treatment and we may note also that the most asymmetrical curves are those associated with the largest expansion during reaction, and therefore the longest chains [compare *e.g.*, Fig. 3].

The complete characterisation of the polymerisation rate in terms

of the chain initiation and propagation rates requires the separate determination of Kn_0 and α which can theoretically be derived from observations of the early stages of the reaction, for it can be shown that the initial slope of the "velocity curve" and the initial acceleration are given by:

$$\frac{d}{dA} \left(\frac{dA}{dt} \right)_{A=A_0} = \frac{1}{3} Kn_0, \quad (10)$$

$$\left(\frac{d^2 A}{dt^2} \right)_{t=0} = 2\alpha K^2 n_0^2 \Delta A. \quad (11)$$

ΔA may also be calculated from observations of the area (A_M) and height $\left(\frac{dA}{dt} \right)_{\max.}$ of the maximum of the velocity curve, but in practise it is found best to attempt only to obtain relative values of α and Kn_0 , since the constants of equations (10) and (11) are altered if equation (7) is replaced by one of the alternative possibilities.

Observations in the neighbourhood of the start of the reaction are necessarily difficult and subject to large errors, so that for most purposes it has been found preferable to characterise the whole reaction in terms of the single constant k_s . For this purpose equation (4) may conveniently be modified by introducing the conditions for the velocity to be a maximum, whence it is easily shown that

$$k_s = \frac{4 \left(\frac{dA}{dt} \right)_{\max.}}{A_\infty - A_0}. \quad (12)$$

This equation has been employed in deriving the polymerisation constants quoted in this communication.

Analysis of the results of a large series of experiments shows that there is a good general correlation between k_s and $\alpha K^2 n_0^2$, which can be expressed approximately by the empirical relationship:

$$k_s^2 \propto (Kn_0)^2 \propto (\alpha Kn_0). \quad (13)$$

This is dimensionally correct and appears to indicate that k_s furnishes a satisfactory measure of the combined initiation (αKn_0) and propagation (Kn_0) velocity constants.

Effects of Temperature and Pressure.

The effect of temperature and pressure on the rate of polymerisation of NO_2 is shown in Fig. 4, in which k_s is plotted as a function of the surface pressure F for three different temperatures. For the lower temperatures the variation with pressure is accurately represented by the equation $k_s \propto F^3$ and this is confirmed by a further series of measurements on substrates containing a catalyst ($CoSO_4$) so that the constants are larger. At $40^\circ C$. however we find an increase of k_s at lower pressures, a phenomenon which appears to be correlated with a phase change, condensed to expanded, occurring within the pressure range 8 to 12 dynes/cm. at $40^\circ C$., but below it at 30 and $35^\circ C$. Measurements of the \bar{F} - A characteristics of films of NO_2 at various temperatures confirm this explanation.

The temperature coefficient and energy of activation can thus only be obtained from the highest pressure (12 dynes/cm.) measurements, in which the material is in the same phase at all temperatures. The observed constants lead to a value for the energy of activation of 20,000

Cals, so that the total variation of k_s with temperature may be written

$k_s = k_0 F^3 e^{-\frac{20,000}{RT}}$ which is of the same form as Semenoff's equation (2).

In addition to this effect on the rate of polymerisation, alteration of temperature and pressure also modify the chain length of the final product. Although it is not at present possible to give an accurate measure of this quantity we can readily determine the manner in which the chain length varies as the conditions are changed. This can be done in two independent ways:

(a) By observation of the total expansion accompanying the reaction. If the areas are referred to a standard pressure, the expansion will be greatest for the longest chains.

(b) By observation of the extent to which the maximum of the curve is displaced. If A_M is the area at which the maximum occurs we may define a quantity ρ given by

$$\rho = \frac{A_M - A_0}{A_\infty - A_0} \quad (14)$$

For a parabola $\rho = 0.50$, while for a reaction which approaches a uni-molecular form $\rho \rightarrow 0$. From the previous analysis, it follows that as the chain length increases ρ will decrease.

These two methods both lead to the conclusion that the chain length of the NO_2 polymers increases with rise of pressure, but is almost independent of temperature over the range 30 – 40°C .

The effects of temperature and pressure on the polymerisation of the unstable peroxide NO_2^1 are more complex. The temperature coefficient has been obtained from a series of measurements at a pressure of 8 dynes/cm., and leads to an approximate value for the energy of activation of 5000 Cals. The principal effect of increasing the pressure is to produce an increase in the size of polymer produced. Reference to Fig. 3 shows that there is a complete change in the shape of the curve, and it is evident that the total expansion is increased and that ρ [equation (14)] is diminished. It may be noted that rise of temperature also leads to an increase in the polymer size.

Fig. 3 shows that there is a complete change in the shape of the curve, and it is evident that the total expansion is increased and that ρ [equation (14)] is diminished. It may be noted that rise of temperature also leads to an increase in the polymer size.

Positive and Negative Catalysts.

A study has been made of the effect of adding various catalytic materials to the aqueous solution under the film, and the results may be illustrated by reference to some experiments with cobalt sulphate and hydroquinone.

Velocity constants for polymerisation of Stable Isomer.

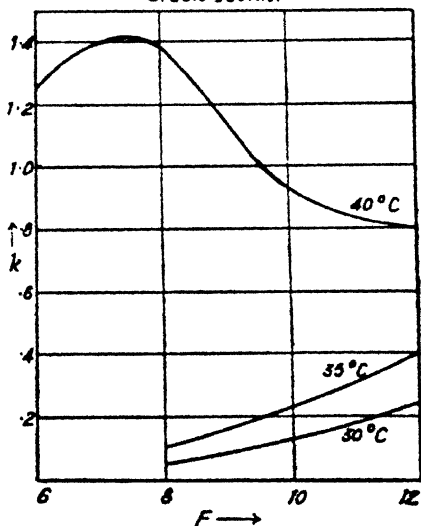


FIG. 4.

Two series of observations on cobalt substrates are worthy of mention. The first is based on experiments in which the oxidation and polymerisation of the glyceride proceed progressively, so that the polymerisation rate is separately determinable [*cf.* Fig. 2].

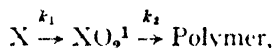
The following results were obtained in this way, for polymerisation at 26° C. and $F = 5$ dynes/cm.:

Concentration of CoSO_4 . . .	10^{-4}	5×10^{-4}	$2 \times 10^{-3}\text{M.}$
Velocity constant (mins. ⁻¹) . .	0.02	0.14	0.38

The second series gives the effect of cobalt on the rate of polymerisation (k_4) of NO_2 at $F = 8$ and 30° C.:

Concentration of CoSO_4 . . .	0	5×10^{-4}	$2 \times 10^{-3}\text{M.}$
Velocity constant (mins. ⁻¹) . .	0.05	0.17	0.33

In both cases a very large catalytic effect is observable. The first evidence of the inhibitory effect of hydroquinone is based on a somewhat different argument. In the course of a series of experiments on the effect of hydroquinone on the rate of oxidation at $F = 11$ dynes/cm. and 2.5° C., it was found that small concentrations (up to 0.001 per cent. in the substrate) had no effect on the oxidation constant, but diminished notably the total expansion associated with the oxidation. Now under these conditions the reaction is essentially



and it is clear therefore that the hydroquinone is inhibiting the second stage of this process, *i.e.*, the polymerisation. Confirmation of this conclusion was obtained by allowing a film to oxidise and isomerise to NO_2 at a low pressure and 35° C., and then injecting hydroquinone into the substrate so as to make the concentration 0.05 per cent. On subsequent compression to $F = 12$ dynes/cm. no reaction was detectable in 20 minutes and thereafter proceeded very slowly, while in the absence of the inhibitor the entire polymerisation would have been complete in 30 minutes.

Polymerisation of Mixed Films.

In the foregoing we have postulated as the final stage in the "drying" of glyceride films a polymerisation process proceeding by a chain mechanism, and perhaps the most direct proof of this conclusion is derived from experiments with mixed films. If the glyceride film be diluted by admixture with a stable ester, such as ethyl myristate we should anticipate that the latter, being unable to take part in the polymerisation chains, should act as an inhibitor. This conclusion is completely borne out by experiment, and reference may be made to Fig. 2, which gives the velocity of oxidation and polymerisation of a mixed film containing 10 per cent. of ethyl myristate at $F = 9$ dynes/cm. Under these conditions the pure glyceride gives almost a linear curve but the retardation of the polymerisation produced by the ester causes the process to split into two fairly well separated consecutive reactions. It should be noted that addition of the ester has no effect on the rate of oxidation: there is indeed no apparent mechanism by which any such inhibition could be produced.

The study of the effect of esters on the polymerisation rate has been greatly extended, and in particular the polymerisation of the stable

isomer XO_2 from numerous mixed films has been investigated. The esters employed have been selected so as to cover a considerable range of degrees of unsaturation, and include in addition to ethyl myristate, triolein, methyl linoleate, ethyl linolenate and methyl β -elæostearate. We are indebted to the British Dyestuffs Corporation for gifts of specimens of the three last named. It was anticipated that an unsaturated ester might prove capable of taking part in the polymerisation chains, so that the inhibitory efficiency would decrease with increasing unsaturation: this is in general confirmed.

Addition of an ester diminished both the rate of polymerisation and also the final complexity of the polymer. This latter conclusion has to be based mainly on the shape of the curves, and the values found for ρ , since there is an inevitable uncertainty in interpreting the areas of mixed films. Variations in the total expansion are therefore not necessarily due to changes in the polymer size.

Thanks are due to Professor E. K. Rideal, the instigator of this work, for much helpful advice and criticism, and to the British Dyestuffs Corporation for material and financial assistance.

Summary.

An account is given of experiments on the "drying" of monolayers of the maleic anhydride compound of β -elæostearin on water, and a mechanism is proposed which recognises the possible existence of two oxidation products of different stability. The polymerisation of both is described and the energies of activation are found to be 5,000 and 20,000 Cals.

It is shown that the observed shapes of the velocity curves can be completely accounted for by assuming that polymerisation proceeds by a chain mechanism in which the chains are terminated by a steric factor.

Two classes of positive and negative catalyst are considered, these being added (a) to the substrate and (b) to the film. In the latter class are a series of esters, which inhibit polymerisation, by breaking the chains, this effect being most marked with a completely saturated ester.

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THE POLYMERISATION OF GASEOUS FORMALDEHYDE AND ACETALDEHYDE.

By J. E. CARRUTHERS AND R. G. W. NORRISH.

Read in Summary on 27th September, 1935.

In the course of experiments on the photo-chemical oxidation of formaldehyde by ultra-violet light of 3000 Å.U., it was found that a rapid reduction of pressure was induced by the light. This reduction of pressure continued on extinguishing the light, although the process of oxidation ceased. No such fall of pressure could be induced in the absence of oxygen. By a process of elimination the effect was traced to a polymerisation of the formaldehyde induced by the formic acid resulting from the photo-chemical oxidation. A similar polymerisation could be effected by the addition of traces of ozone to the formaldehyde in the dark, and here again formic acid was responsible.

It was then found that the addition of a few per cent. of formic acid in the dark to gaseous formaldehyde at about 500 mm. pressure induced a rapid polymerisation, the velocity of which was some hundred-fold greater than in the case of pure formaldehyde. The results indicate that we have here a promoter for the reaction in the gas phase enormously more powerful than anything which has hitherto been described. In the present paper we have undertaken a study of the kinetics of the process, and it is evident that we have to deal with a branching chain mechanism, in which both the initiation and branching of chains are dependent upon the formic acid. The process, however, is confined to the surface of the vessel, and we are thus concerned with the kinetics of a chain reaction in a heterogeneous system. It is interesting to note¹ that Spence has concluded that the polymerisation of liquid monomeric formaldehyde occurs by way of a chain reaction at a heterogeneous surface, and can in certain cases become explosive. In his case curious threadlike growths of the polymer developed at the surface of the vessel, and in our own case we have noticed similar formations.

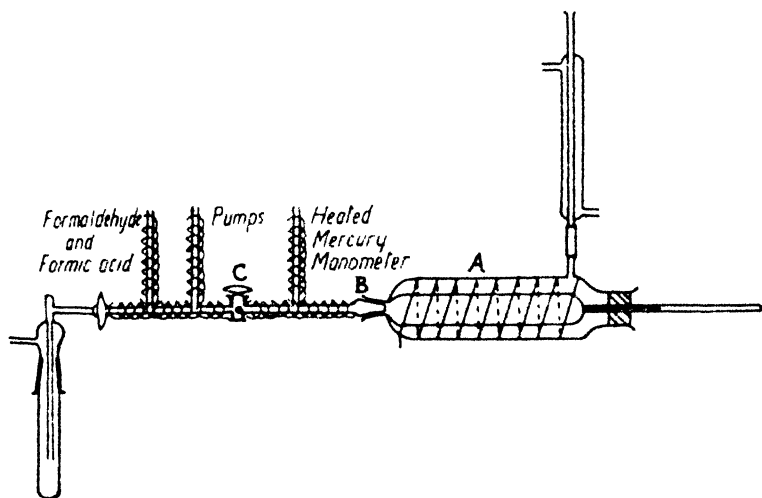


FIG. 1.

The polymer itself has the physical properties of the polyoxymethylenes described by Auerbach,² and it is readily depolymerised by heating. We conclude that it has the essential structure suggested by Staudinger, for there is little doubt in view of the easy depolymerisation that the formaldehyde units are joined through oxygen atoms rather than by C—C linkages. Staudinger has shown how molecules of polyoxymethylene in aqueous media may increase in length by a chain process catalysed by hydroxyl groups or hydrogen ions; our own results suggest that in the case of the gas, similar polyoxymethylene chains can be built up at the surface, and that for this process the formic acid is a powerful promoter. Its exceptional efficiency operates through its power of producing branching chains, and we shall show in the discussion below that this conception is in full accord with the theory of Staudinger. Similar results have been obtained for the polymerisation

¹ *J.C.S.*, 1933, 1193; 1935, 506.

² *Arb. Kais. Gesundh.*, 1907, 22, 584, etc.

of acetaldehyde by formic acid, and the polymerisation of formaldehyde by acetic acid, though in the case of mixtures of acetaldehyde and acetic acid no effect could be observed. With glyoxal and formic acid the process appeared to stop short with a simple addition reaction between the two molecules.

Experimental.

The first apparatus used is shown in Fig. 1. The reaction vessel consisted of a double-walled quartz tube of 130 c.c. capacity containing a quantity of water in the outer jacket, which was kept boiling by heating electrically. The inner vessel was attached by a ground glass joint to a mercury manometer and a tap leading to supplies of formic acid and

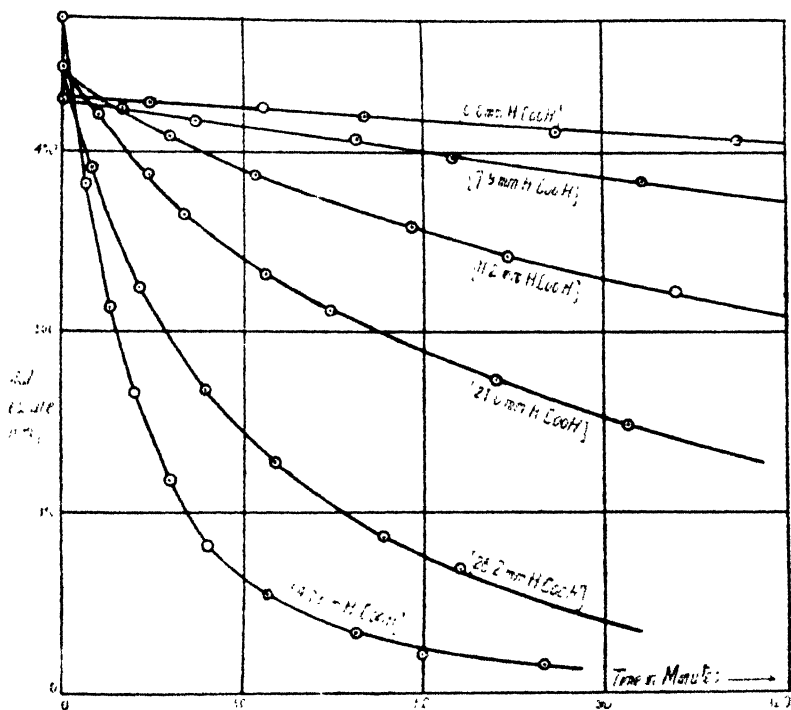


FIG. 2.

formaldehyde and to a mercury pump for evacuating. The formic acid was prepared by the standard method of H. Erdmann³ and kept at room temperature in the liquid condition. The formaldehyde was prepared by the method of Trautz and Ufer⁴ and stored in a trap surrounded by liquid air. Before use the formic acid was evacuated several times at -78°C . (mixture of solid carbon dioxide and ether) to remove all traces of air. The connecting tubing up to the reaction vessel and the manometer was wound with nichrome wire and asbestos tape and kept electrically heated to about 90° . The manometer itself was similarly wound with nichrome wire and protected by a concentric glass tube and heated to the same temperature.

³ *Vanino Preparative Chemie II*, Stuttgart, 1923, p. 101.

⁴ *J. prakt. chem.*, 1926, 105.

The taps and ground joint were lubricated with Apiezon grease "N" and were the only parts of the apparatus that remained cool. In order

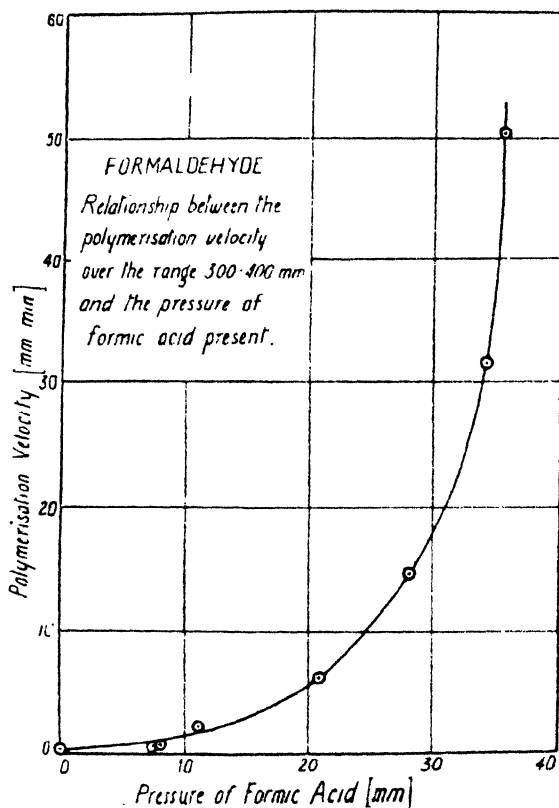


Fig. 3.

It is seen that an enormous increase of velocity was observed at pressures of formic acid approaching 35 mm.

Series II.—Estimation of Formic Acid during the process of Polymerisation.*

A series of experiments was carried out starting with 500 mm. of formaldehyde and a fixed amount (30 mm.) of formic acid. The contents of the reaction vessel were condensed into a detachable liquid air trap at different stages of the reaction. This was then removed and water added; the resulting solution of formic acid was titrated with *N*/100 soda, using phenolphthalein as indicator. A blank run with pure formic acid showed that 30 mm. were equivalent to 14.1 c.c. of *N*/100 soda. In Table I. the results are shown and from

TABLE I.

Pressure of Formaldehyde.	Volume of <i>N</i> /100 Soda Required.	Pressure of Formic Acid.
400 mm.	14.1 c.c.	30 mm.
296 mm.	10.65 c.c.	22.6 mm.
224 mm.	8.2 c.c.	17.5 mm.
108 mm.	4.2 c.c.	8.9 mm.
9 mm.	3.8 c.c.	8.0 mm.

* The results described in this section correct an error in our preliminary note. (*Nature*, 1935, 135, 582.)

to carry out an experiment the whole apparatus was first evacuated, formic acid was introduced to the desired pressure and then the formaldehyde.

Series I. Reaction Rates.

The pressure of formaldehyde was fixed at 500 mm. and the rates of polymerisation observed for pressures of formic acid from 0.35 mm., the upper limit being fixed by the vapour pressure of the formic acid. Readings were taken every few minutes; results are shown in Fig. 2.

In Fig. 3 are plotted the reaction rates during the period of reaction corresponding to a pressure change of 500-400 mm.—as a function of the pressure of formic acid.

the plot in Fig. 4, it will be seen that there is nearly a linear relationship between the pressure of formic acid and of formaldehyde during the whole course of the polymerisation.

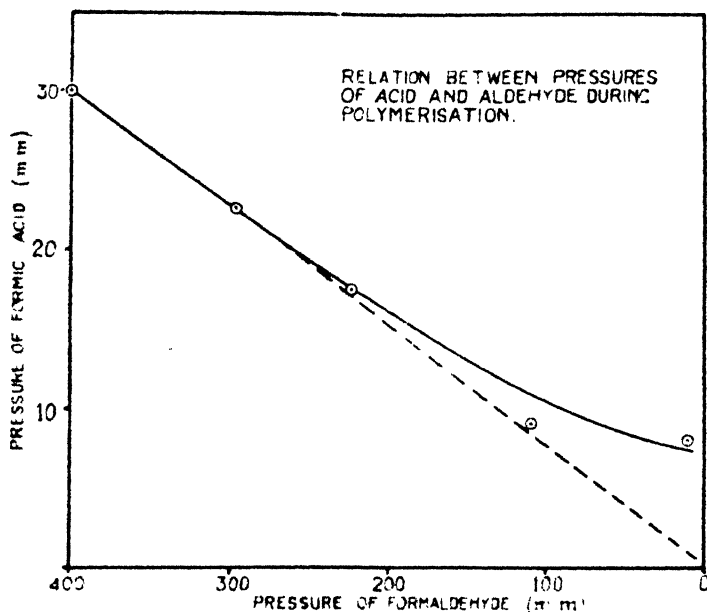


FIG. 4.

Series III.—Experiments with Completely Heated Vessel.

The apparatus used for the experiments of Series I. and II. contained a stopcock and a ground joint connecting the quartz reaction vessel to the

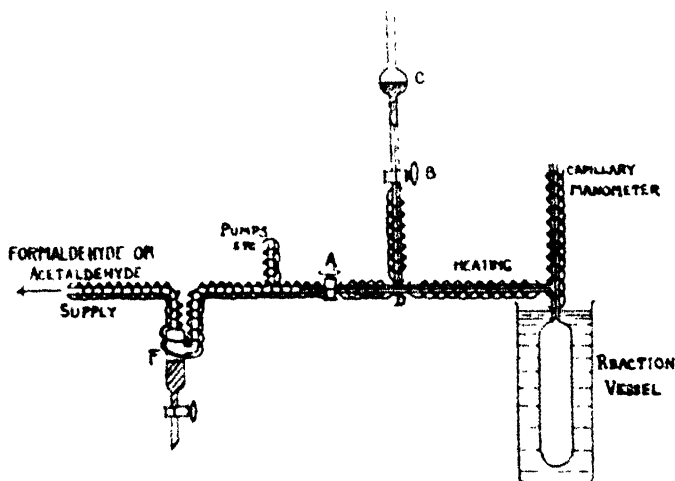


FIG. 5.

glass portion of the apparatus. Neither of these parts could be directly heated and it was observed that the polymer separated at the cold part.

Experiments were now carried out in a completely heated system

(see Fig. 5), so that it was possible to assess the importance of these cold portions of the apparatus. The difficulty of the ground joint was overcome by using a system made entirely of glass, but there still remained

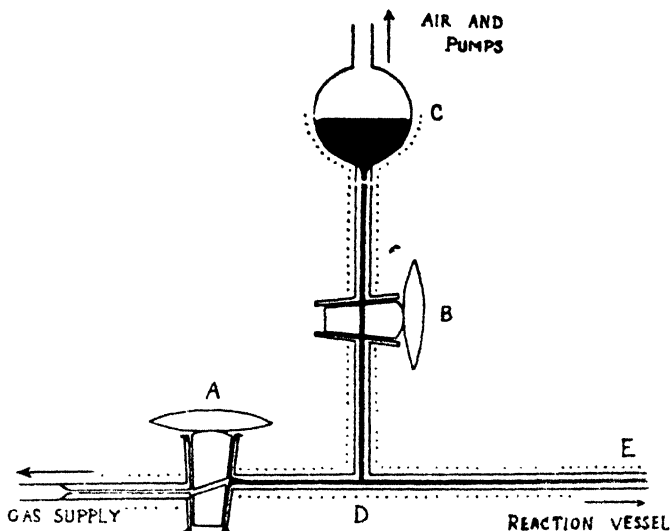


FIG. 6.

the problem of the cold part in the neighbourhood of the stopcock. The device illustrated in Fig. 6 provided a solution. The principle was to have a thread of hot mercury from the tap A up to the gas in the capillary leading to the reaction vessel. This eliminated all the cold portions of the apparatus.

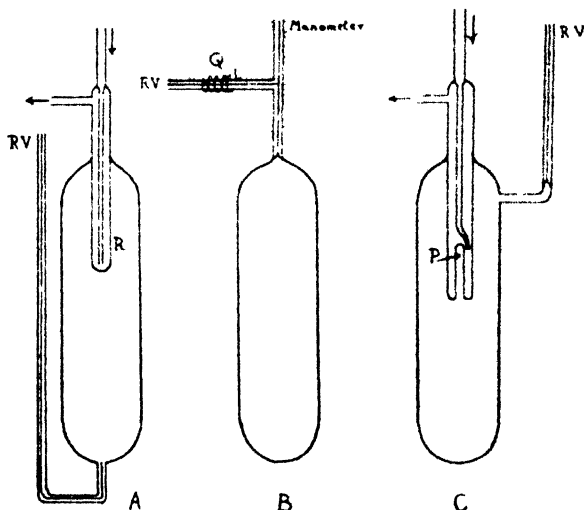


FIG. 7.

The method of operation of the mercury "cut-off" was as follows: first of all the reaction mixture was introduced into the reaction vessel in the usual way, through tap A,—tap B being closed. A was then closed and by opening B, a thread of mercury allowed to enter the capillary BDE. The small amount of gas trapped in AD was removed by the

pump on carefully opening A.

In the completely heated system no polymerisation took place in 300 mm. of formaldehyde, even when 32.4 mm. of formic acid were present. It was first thought that this stability was possibly due to the fact that the vessel was new and consequently that the surface was not

"matured." The reaction vessel was allowed to cool slightly, thus depositing a layer of polymer on the surface. On introducing more formaldehyde, however, there was practically no polymerisation.

A further experiment in which the hot vessel was packed with quartz and glass tubing similarly showed no polymerisation.

These experiments led us to the view that the polymerisation observed in experiments with formaldehyde required the presence of a cold surface where the polymer could be deposited.

Series IV.—Vessels with Cooled Surfaces.

Construction of new types of reaction vessels enabled the influence of a cooled surface to be tested.

In A, Fig. 7, cooling was effected by a flow of cold water, in a manner seen from the diagram, the area of cooled surface being about 10.5 sq. cms. The whole of the other portion of the reaction vessel was heated to 100°C by immersion in boiling water, and the tubing heated electrically as before. The procedure was to introduce the gas into the hot reaction vessel, and then to turn on the cooling water after the initial reading of pressure had been observed.

Fig. 8 shows the results of experiments carried out with this cooled surface. The decrease of pressure, due to cooling of the gas when the cold surface is introduced at the beginning is small—as is seen for example, in curve 1 of Fig. 8.

The important observation arising from these experiments is that although we have a considerable area of cold surface and although the initial rate of polymerisation is very rapid, yet the pressure does not fall to zero. This means that in this case we must have an equilibrium between formaldehyde gas and polymer. The position of the equilibrium depends on the pressure of formic acid present, being more and more in favour of polymerisation as the pressure of formic acid is increased.

When, however, an element of volume of the system, adjacent to the surface was cooled as in B (Fig. 7) in which a section of the capillary was kept cool with water, or in C (Fig. 7) in which a small cooled space P was provided in the centre of the reaction vessel it was found that the polymerisation was complete and no equilibrium was observed. From this we may conclude that if the cooled surface is in contact with the hot gas, partial depolymerisation leading to equilibrium occurs but that if the

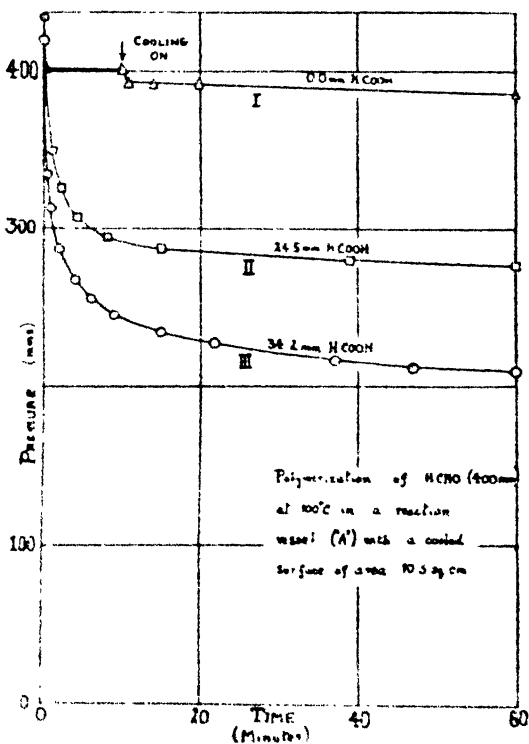


FIG. 8

cooled surface be in contact with cold gas there is no depolymerisation and the reaction proceeds to completion.

Series V.—Experiments at 18° C.

Experiments at room temperature have shown that the promoting influence of formic acid is as strongly marked at 18° C. as at 100° C. The rate of polymerisation of the pure gas is greater at the lower temperature but even so, the reaction rate is tremendously accelerated when 21 mm. of formic acid are added to 400 mm. of formaldehyde (see Fig. 9) and polymerisation is complete in forty minutes.

In these experiments the reaction vessel only was maintained at 18° C., the connecting tubing and manometer being heated electrically as before.

Examination of the Polymer.—The polymer which is deposited either at 18° C. or at 100° C. is a white powder insoluble in water on heating, and insoluble in alcohol and ether. The solid melts over a range of temperature, the mean being about 157° C.

It appears to be of similar nature to the insoluble polyoxymethylenes described by Auerbach² and Staudinger.³

Order of Reaction.

—An analysis of the data represented in the curves of Figs. 2 and 8 shows that the polymerisation reaction both with the vessel at 18° C. and also at 100° C. is approximately of the second order. Examples are given in Table II, where the concentrations are expressed in mm. for calculation of k_{11} .

The bimolecular constants have been calculated from point to point in the curves. These results when coupled with the data of Series II

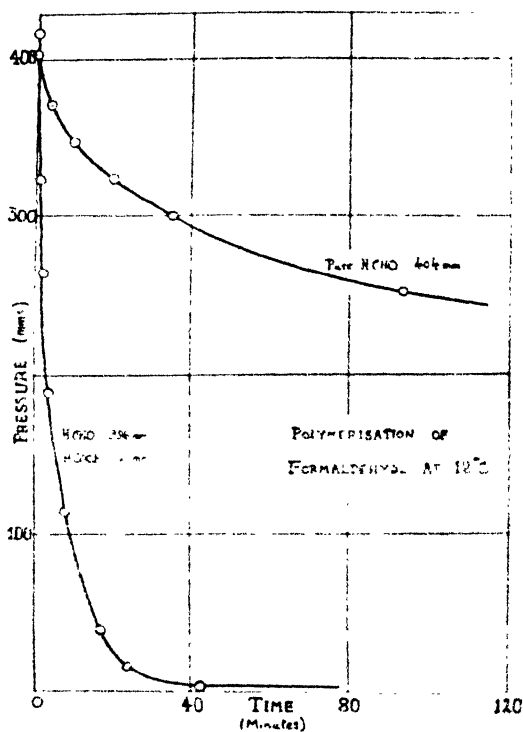


FIG. 9.

are of peculiar interest when it is remembered that the pressure of formic acid is falling progressively throughout the run. Its significance will be seen in the discussion of the kinetics below.

Series VI.—Polymerisation of Gaseous Acetaldehyde.

In view of the action of formic acid on the polymerisation of formaldehyde, experiments were carried out in an attempt to find if an analogous reaction occurred in the case of acetaldehyde. Observations were made both at 100° and 20° using reaction vessel B (Fig. 7). It was found at 100° C. formic acid had no effect on acetaldehyde. At 20° however, there

² Z. physik. Chem., 1927, 126, 425.

TABLE II.*

<i>t.</i>	<i>p.</i>	<i>k.</i>	<i>t.</i>	<i>p.</i>	<i>k.</i>	<i>t.</i>	<i>p.</i>	<i>k.</i>
(Pressure of Formic Acid = 35.7 mm. Temperature = 100° C.)								
0	0.20	0.14	6	3.47	0.26	12	2.35	0.22
2	5.29	0.24	8	2.95	0.24	14	2.14	0.18
4	4.24	0.20	10	2.00	0.21			
(Pressure of Formic Acid = 21.0 mm. Temperature = 100° C.)								
0	5.00	2.04	50	2.85	2.94	100	1.93	4.06
10	4.46	3.43	60	2.63	5.30	110	1.79	4.38
20	3.78	2.52	70	2.42	5.32	120	1.66	3.86
30	3.39	2.71	80	2.24	3.44	130	1.56	5.83
40	3.08	2.92	90	2.08	3.74			
(Pressure of Formic Acid = 11.2 mm. Temperature = 100° C.)								
0	5.10	1.18	40	4.10	1.62	80	3.57	1.00
10	4.81	1.14	50	3.99	0.91	90	3.44	0.87
20	4.56	1.06	60	3.85	1.05	100	3.34	0.83
30	4.35	1.05	70	3.70	0.68	110	3.25	0.88
(Pressure of Formic Acid = 2.1 mm. Temperature = 18° C.)								
0	1.17	0.025	3	2.20	0.77	5	1.98	0.80
1	1.25	0.090	4	1.88	0.94	6	1.48	0.93
2	1.04	0.175						

* Time (minutes) = *t*; Pressure (mm.) = *p*; $k \times 10^3 = \kappa$.

was a rapid polymerisation showing a striking similarity to that found with formaldehyde. At this temperature pure acetaldehyde vapour was completely stable, while the addition of formic acid up to about 25 mm. pressure caused a rapid polymerisation. With a packed vessel the rate of polymerisation was still greater. Results are shown in Fig. 10. The increase of reaction velocity in the packed vessel is roughly in proportion to the increase of surface and it is apparent that the polymerisation of acetaldehyde is again a heterogeneous reaction.

Although the effect of the formic acid is numerically not quite so great in the case of acetaldehyde as it is with formaldehyde, yet the curves of Figs. 3 and 10 are of the same form and in acetaldehyde we see the same tendency for a very rapid increase in the rate of polymerisation as the pressure of formic acid reaches a limiting value.

Series VII. Experiments with other Substances.

The effect of water and acetic acid on the polymerisation of formaldehyde at 100° C. was measured in the apparatus used in Series I., and the results are shown in comparison in Fig. 11. It will be seen that whereas the acetic acid produces an induced polymerisation of the same order of magnitude as formic acid, the effect of water is very small. On the other hand, experiments with acetaldehyde, show that acetic acid has no observable polymerising effect either at 100° C. or 20° C.

Series VIII.—Experiments with Glyoxal.

Using monomeric glyoxal prepared by the method of Harries and Temme⁶ it was found that glyoxal in the presence of formic acid in the

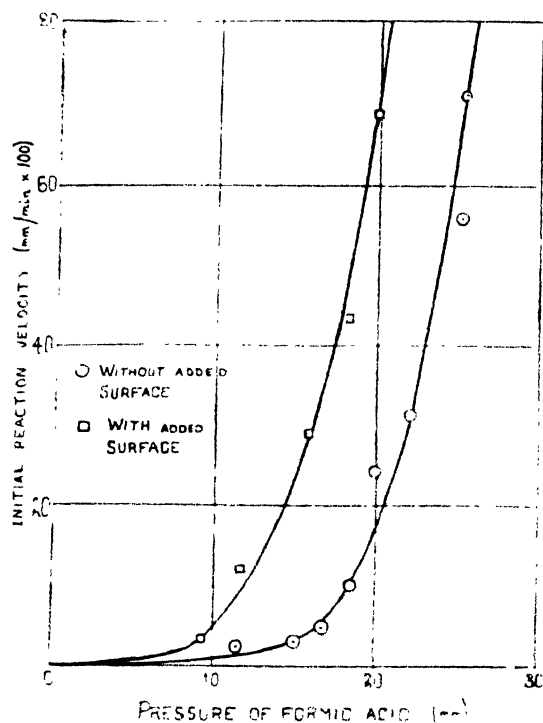


FIG. 10.

rate of polymerisation as a function of the pressure of formic acid is characteristic of a chain reaction. As the pressure of formic acid approaches 35 mm., the velocity increases in such a manner as to suggest that the reaction is about to become explosive. The form of the curve can be represented by the empirical relation:

$$\text{Rate} = \frac{A(\text{H. COOH})}{B - (\text{H. COOH})}$$

This is seen by reference to Table III.

From the experiments recorded in Series II, however, it will be seen that the disappearance of the formic acid is closely related to the disappearance of the formaldehyde,

vapour state does not exhibit the phenomenon of induced polymerisation shown in the case of formaldehyde but that it appears to form a condensation product directly with the formic acid. Thus by addition of excess of glyoxal to formic acid a rapid reduction of pressure occurred and the pressure of glyoxal then remained unchanged. The experiments were not prosecuted in detail but it appeared that the two substances reacted in about equimolecular proportions.

Discussion.**Kinetics of the Reactions.**

The curve shown in Fig. 3 for an approximately fixed concentration of formaldehyde representing the

TABLE III.

$$A = 4.5 \quad B = 39.$$

Pressure of Formic Acid.	Velocity Observed (from Curve of Figure 3).	Velocity Calculated.
5 mm.	0.9 mm./min.	0.7 mm./min.
10 "	1.4 "	1.55 "
15 "	3.0 "	2.8 "
20 "	5.4 "	4.75 "
25 "	10.1 "	8.05 "
30 "	17.6 "	15.0 "
33 "	30.0 "	29.5 "
35 "	40.0 "	39.5 "
36 "	50.0 "	54.0 "

⁶ Ber., 1907, 40, 105.

and that at all times during the reaction an approximately constant ratio is maintained between the concentrations of the two substances. Further, an investigation of the order of reaction throughout the course of a given run shows that the polymerisation remains bimolecular with reference to the formaldehyde.

The interpretation of these facts may be readily obtained if it be assumed that the polymerisation occurs at active centres generated (1) by a primary process dependent upon the reaction of formaldehyde with formic acid in the gas phase (2) by a branching process arising from the encounter between formic acid and an already existing centre, and extinguished by their reaction with formaldehyde.

Thus, writing (n) for the stationary concentration of centres we obtain

$$\frac{dn}{dt} = k_1(\text{acid})(\text{ald}) + k_2n(\text{acid}) - k_3n(\text{ald}) = 0.$$

Whence

$$n = \frac{k_1(\text{acid})(\text{ald})}{(k_3)(\text{ald}) - k_2(\text{acid})} \quad (1)$$

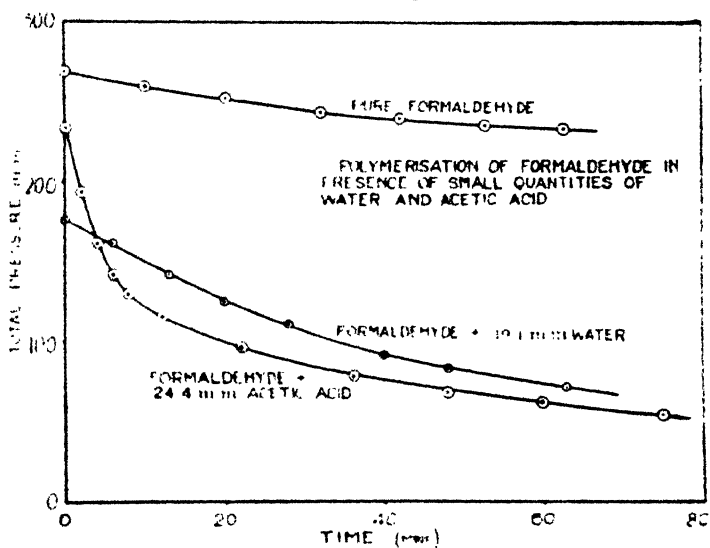


FIG. 11.

The rate of polymerisation of aldehyde is given by $k_3n(\text{ald})$.

$$\text{Whence} \quad -\frac{d(\text{ald})}{dt} = \frac{k_1k_3(\text{acid})(\text{ald})^2}{k_3(\text{ald}) - k_2(\text{acid})} \quad (2)$$

This equation is in agreement with the empirical expression obtained from the results of Series I for a constant pressure of formaldehyde.

Assuming that a molecule of formic acid disappears at each formation of a new chain, by the branching process and ignoring the comparatively small removal by the primary reaction, the rate of loss of formic acid is given by

$$\begin{aligned} -\frac{d(\text{acid})}{dt} &= k_2n(\text{acid}) \\ &= \frac{k_2k_1(\text{acid})^2(\text{ald})}{k_3(\text{ald}) - k_2(\text{acid})} \quad (3) \end{aligned}$$

Dividing equation (2) by equation (3), we obtain

$$\frac{d(\text{ald})}{d(\text{acid})} = \frac{k_3(\text{ald})}{k_2(\text{acid})} \quad (4)$$

Whence by integration

$$(\text{ald}) = C(\text{acid})^{k_3/k_2},$$

and thus that if

$$\begin{aligned} k_3 &\sim k_2 \\ (\text{ald}) &= C(\text{acid}) \end{aligned} \quad (5)$$

in accordance with the results of Series II.

By combining expressions (2) and (5) for any one particular run, we obtain

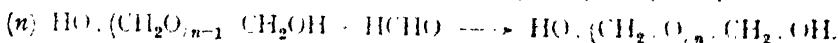
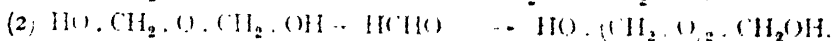
$$-\frac{d(\text{ald})}{dt} = \frac{k_1 k_3}{k_3 - k_2} (\text{ald})^2.$$

Thus it follows that the order of the polymerisation reaction is approximately bimolecular in accordance with the data of Tables II. and III.

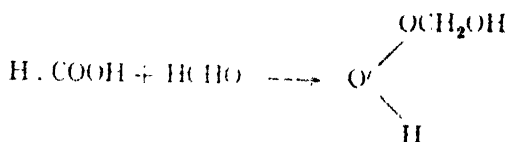
From the experiments of Series III. in a completely heated system, it is clear that the rate of depolymerisation is greater than that of polymerisation, for no fall of pressure could be observed even with packed vessels and high pressure of formic acid. Upon the introduction of a cooled surface, however, the polymerisation reaction immediately took place. If this cooled surface was exposed to the bombardment of the hot gas partial depolymerisation occurred, and thus an equilibrium pressure was reached; but if the cooled portion was isolated in a side capillary, then in this part there was no depolymerisation, and reaction therefore proceeded to completion.

Mechanism of the Process.

Staudinger has visualised the initiation of chains in aqueous solvents as dependent on the primary production of dihydroxymethylene from formaldehyde and water. The chains are propagated in the following manner, with the production of polyoxymethylenes.

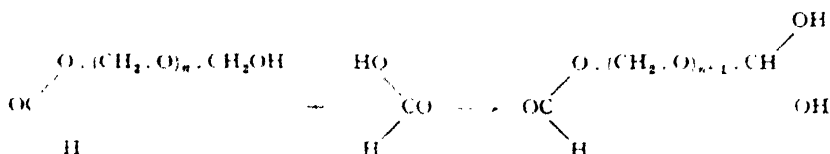


We conceive that in our case the function of the formic acid is to generate in the gas phase a compound analogous to the dihydroxymethylene, namely the monoformic ester of dihydroxymethylene as represented by the equation:



From this, polymerisation chains can grow by the reaction of the hydroxyl group, and the product will separate at the cold surface of the vessel. This constitutes the primary process referred to above.

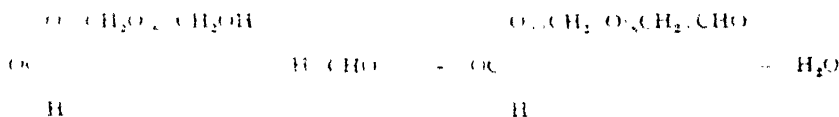
It will be observed, however, that instead of the addition of formaldehyde to the polymerising chain, an addition of formic acid may occur, and this process will produce two terminal hydroxyl groups.



From each of these hydroxyl groups a new chain of polymerisation can be propagated. In this way, we may visualise the branching mechanism referred to above, in which a formic acid molecule is removed by reaction with a centre of polymerisation and generates two new centres thereby.

If the probabilities of the fixing of formaldehyde and formic acid by the polymerisation process are roughly equal, the requirements of equation (5) are fulfilled. It will then follow that the pressure of formic acid remains approximately proportional to the pressure of formaldehyde throughout the course of a given run.

The extinction of the reaction centres was represented as dependent on formaldehyde in terms of an alternative reaction between the centre and an aldehyde molecule. This would occur if instead of the formation of an addition compound a condensation product were produced.



In this case the aldehyde group terminates the chain, which in the absence of the hydroxyl group, cannot be propagated further.

This mechanism faithfully conforms to the requirements of the kinetic hypothesis developed above. It represents the starting and branching of reaction chains as dependent on formic acid and their extinction dependent on the formaldehyde. In addition, it introduces into the mechanism of Staudinger for the formation of large polyoxymethylene molecules the possibility of the formation of branching chains. It is this fact which accounts for the enormous promoting activity of the formaldehyde, as compared with other polymerising agents which are only able to initiate straight chains, without the possibility of branching.

A process of this kind would tend to give rise to thread-like molecules, branching at intervals, and ultimately if the growth continued long enough to an intertwined network. This structure might be considered as a basis for the gel formation in monomeric liquid formaldehyde described by Spence.¹ In this connection, it is also of interest that Spence has described an apparent explosive polymerisation of the liquid, with evolution of heat. Such a process must undoubtedly occur by a branching chain mechanism, and on the above theory would be readily catalysed by the presence of formic acid. It is significant that Spence found that the stability of monomeric liquid formaldehyde depended upon its freedom from oxygen, and since the interaction of oxygen with formaldehyde undoubtedly tends to produce formic acid, it is tempting to conclude that the stability of the liquid is in effect bound up with its freedom from formic acid.

The rapid polymerisation of formaldehyde by acetic acid and of acetaldehyde by formic acid (Series VI. and VII.) has been shown to be apparently identical with the polymerisation of formaldehyde by formic acid. It will be seen that simply by the substitution of CH_3 for H in the formulæ, the kinetics of these reactions may be explained by an entirely analogous mechanism to that developed above. No polymerisation, however, is induced by acetic acid in acetaldehyde, and it may be concluded that the first stage in the chain is unable to take place, and that there is no tendency to form an addition compound between acetaldehyde and acetic acid. With glyoxal, on the other hand, some sort of compound with formic acid is clearly formed, but there is no propagation of a reaction chain, a circumstance which might be explained by the absence of a hydroxyl group in the structure of the product. The matter, however, awaits further investigation.

Summary.

1. It is shown that the polymerisation of monomeric formaldehyde vapour both at 100° and at 18° C. is subject to a marked promotion by the presence of relatively small quantities of formic acid.
2. As the pressure of formic acid is increased the rate of polymerisation at 100° C. increases to such an extent as to indicate that it will become infinitely large at pressures of formic acid beyond about 40 mm.
3. The formic acid disappears during a given run at a rate which throughout is nearly proportional to the rate of removal of formaldehyde.
4. During a given run the polymerisation is bimolecular with reference to the formaldehyde.
5. With a vessel completely heated to 100° C. there is no polymerisation, even with 30 mm. of formic acid.
6. The process is heterogeneous and occurs at some element of cold surface. If the cold surface be surrounded by a volume element which is also cold, the polymerisation goes to completion. If, however, the cold surface be exposed to the bombardment of the hot gas there is sufficient depolymerisation to cause an equilibrium. When the whole surface is at 100° C. the rate of depolymerisation is so much greater than the rate of polymerisation that there is no measurable reaction.
7. Similar results are obtained with formaldehyde and acetic acid, and acetaldehyde and formic acid, but with acetaldehyde and acetic acid, and glyoxal and formic acid there is no polymerisation.
8. The above results are explained on the basis of a branching chain mechanism in which the formic acid is responsible both for starting and branching the chains, while the extinction of chains occurs by an alternative reaction with formaldehyde.
9. The process may be visualised by an extension of the theory of Staudinger in which polyoxymethylene chains originate from the hydroxyl group of the formic acid. The high efficiency of the formic acid as a promoter is then explained by its addition to the polyoxymethylene chain, with the production of two hydroxyl groups and consequent branching.
10. The bearing of these results on the polymerisation of monomeric liquid formaldehyde is discussed.

We are indebted to the Department of Scientific and Industrial Research, and to the Governing Body of Emmanuel College, Cambridge, for maintenance grants to one of us (J. E. C.), and to the Royal Society and the Chemical Society for grants for apparatus.

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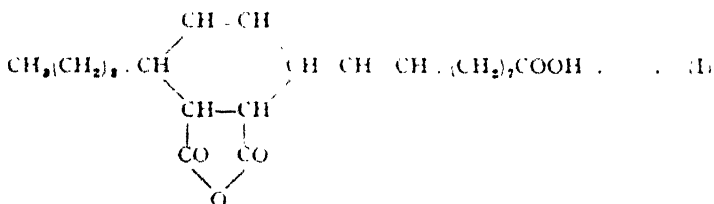
RECENT INVESTIGATIONS INTO THE DRYING OF OILS AND RELATED UNSATURATED COMPOUNDS.

BY R. S. MORRELL AND W. R. DAVIS.

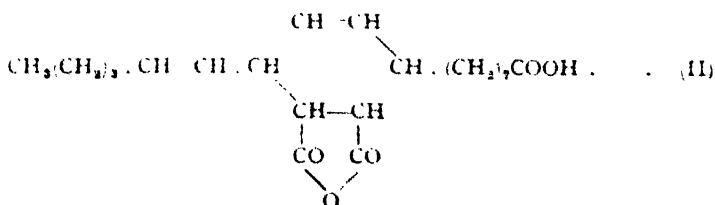
The chemical and physical changes that occur during the drying of an oil can be studied with greater accuracy in pure compounds of suitable structure than in the complex mixture of glycerides found in the natural oil.

Two classes of complex formed from maleic anhydride and α and β elæostearic acids and their two respective triglycerides have recently been the subject of an investigation which has thrown further light on the "drying" process. A preliminary observation that the maleic anhydride compound of β elæostearin would set to a hard film in about twelve hours at room temperature or one hour at 100°C ., whilst the corresponding maleic anhydride compound of α elæostearin remained fluid for several weeks, suggested these compounds as a profitable field of investigation.

Combination between maleic anhydride and α and β elæostearic acids or their triglycerides can be carried out quantitatively to give compounds of the following structure.¹



α elæostearic acid maleic anhydride compound.



β elæostearic acid maleic anhydride compound.

It is of interest to note that with α and β elæostearic acids two possible combinations with maleic anhydride exist for each isomer. Since the acid contains three conjugated double bonds either of two pairs might react with maleic anhydride according to the Diels-Alder system.² Actually only one combination product is formed for the α acid and one for the β acid, there being no experimental evidence for the existence of mixtures. Examination of the atomic models of the

¹ Morrell and Samuels, *J.C.S.*, 1932, 2251.

² Cf. Farmer, *Ann. Reports Chem. Soc.*, 1930, 88.

eight possible *cis* : *trans* isomers of this acid shows that on the assumption that stearic hindrance occurs due to the terminal hydrocarbon chains, the carboxyl groups and the hydrogen atoms, the following types of combination are favoured structurally:—

<i>Isomers of elaeostearic acid</i> C = <i>cis</i> ; T = <i>trans</i> .	<i>Type of maleic anhydride</i> <i>addition compound.</i>
T. T. T.	Mixture of α and β compounds.
T. C. T.	Mixture of α and β compounds.
T. T. C.	α compound possible
C. T. T.	β compound possible.
T. C. C.	α compound most probable.
C. C. T.	β compound most probable.
C. T. C.	No reaction likely.
C. C. C.	No reaction likely.

In the above table an α compound (I) is designated as one in which the two ethenoid linkages most remote from the carboxyl radical are involved in the reaction and a β compound (II) that in which the two near to the carboxyl radical react. α and β elaeostearic acids give, therefore, typical α and β maleic anhydride compounds respectively and on this evidence the α acid is probably of T. C. C. and the β of C. C. T. structure.

Oxidation experiments have been undertaken with solutions of these compounds whereby the amount of oxygen absorbed by the compound was followed conjointly with determinations of peroxide value, iodine value and viscosity, the last being a means of following the association of the oxidised molecules. The final oxidation product, after isolation from the solvent, was subjected to a more exhaustive chemical examination to confirm the structure of the oxidised molecule.

The choice of a suitable solvent as a medium for these experiments became a matter of great importance. Preliminary work showed that the amount of association consequent upon oxidation was closely related to the polarity of the solvent. Polar solvents were shown to restrict, whilst non-polar solvents favoured, molecular aggregation and in liquids of low dielectric constant, such as carbon tetrachloride and benzene, the majority of the oxidation product was precipitated as a gel within a few hours of oxidation. Glacial acetic acid and certain polar solvents, however, restricted the aggregation sufficiently to maintain a soluble polymer, glacial acetic acid being the most favourable for experiment. From the experiments in non-polar solvents was revealed the property of a precipitated gel to carry down with it any metallic catalyst used to assist oxidation. The oxidation process invariably came to a standstill after an oxidised gel had been precipitated and only recommenced on further additions of catalyst. Whether chemical or physical forces are responsible for this addition of the catalyst to the gel has not been decided, but adsorption forces would seem to be indicated.

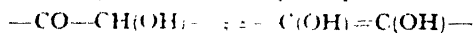
Oxidation in benzene solution could only be carried out when catalysed, cobalt salts being the most suitable for this purpose. Oxidation in glacial acetic acid proceeded without the aid of a catalyst and only towards the end of the oxidation was the presence of a cobalt "drier" advisable to complete the oxygen absorption. It would seem as though in benzene the molecules were so oriented at the liquid gas interface as to have their reactive centres buried in the liquid away from the oxygen and one of the functions of the catalyst was to redispense this arrangement. This orienting influence of metallic bodies is considered by P. Slansky¹ where he advances the theory that basic catalyst such as lead oxide will draw the

¹ *Chem. Umschau*, 1924, 31, 277.

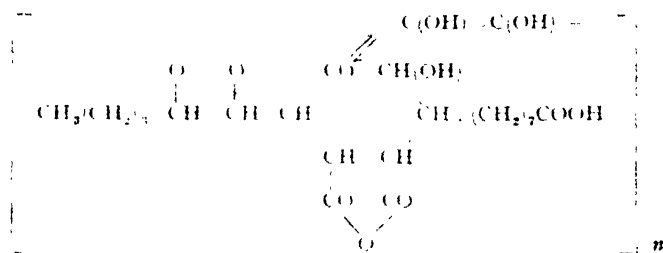
glyceryl radical of a surface molecule inwards towards the body of the compound thereby exposing the unsaturated acid chains to oxidation at the surface. In contrast is the function of carbon black, which becomes adsorbed on the unsaturated acid chains and holds them inwards away from the surface and in consequence reduces the amount of oxidation.

The so-called autocatalytic oxidation was noticed in all the experiments and the oxygen absorption/time curves were of the usual type for this process.

The final oxidation products of the β compounds (acid and glyceride) were such that both ethenoid linkages acquired two atoms of oxygen each. These two oxidised linkages were nevertheless markedly different in character, that in the aliphatic chain section of the molecule being peroxidic in structure, while that in the hydrobenzene ring showed a tautomeric equilibrium mixture of keto-hydroxy and di-hydroxy forms, *i.e.*



The formula of completely oxidised β elaeostearic acid maleic anhydride compound is

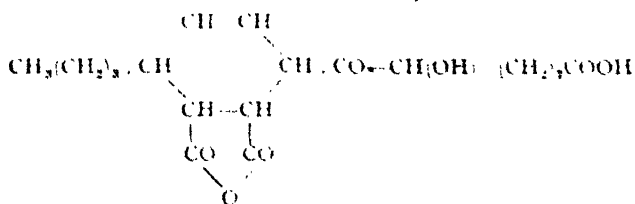


The oxidised glyceride has a corresponding structure,

From examination of the graphs of the oxidation process the peroxide radical appeared to be mainly, if not solely, responsible for the molecular association. The curve in Fig. 1 shows how the final equilibrium condition of the oxidised solution of β elastearin maleic anhydride compound in glacial acetic acid was reached by way of related changes in unassociated peroxide content and viscosity. As the unassociated peroxide content fell, i.e., the peroxides associated, the viscosity rose until a final equilibrium condition was reached concurrently in both properties.

The α acid compound confirmed the hypothesis that the peroxide radical was solely responsible for association at ordinary temperatures. Here, only the ethenoid linkage in the aliphatic chain would oxidise, the product being of ketohydroxy structure ($-\text{CO}-\text{CH}(\text{OH})-$) and unassociated. No peroxide could be detected. The absence of molecular association was amply evidenced from (1) the unchanged viscosity of the oxidised and unoxidised solutions, and (2) molecular weight determinations by the cryoscopic method on the isolated oxidation product.

The structure of the oxidised α acid compound is :

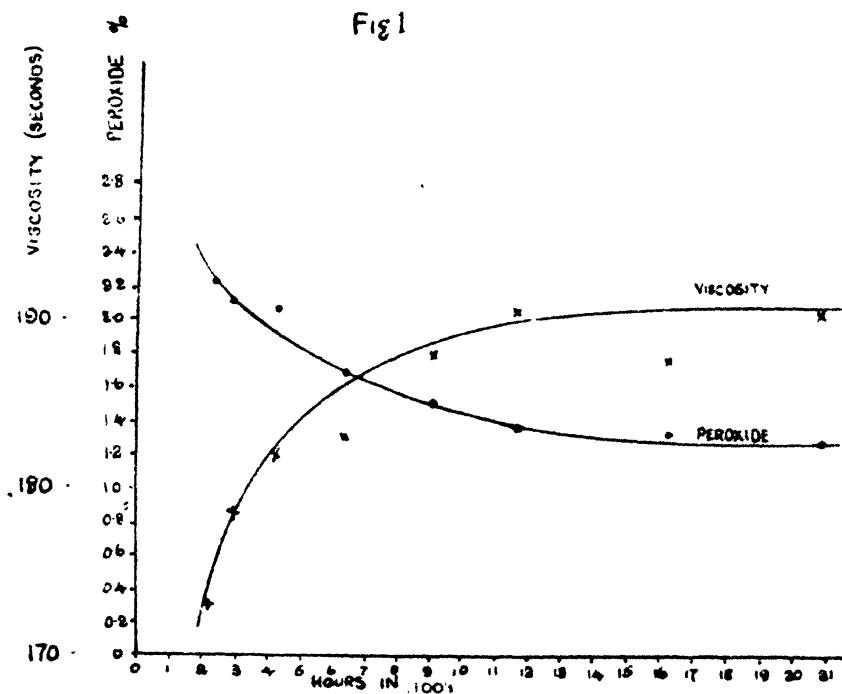


The triglyceride has a corresponding structure.

The stability of the peroxide radical in the β glyceride compound, when produced at ordinary temperatures in non-polar solvents, is notable. The peroxide value remained unchanged at the theoretical figure for one peroxide grouping per molecule for 12 months. (The difference in the peroxide values of gels produced in polar and non-polar solvents is referred to later.)

The marked restriction that polar solvents have on the association of the oxidised β compounds has been mentioned on page 210; the influence of the solvent, however, extends further than the rate of association and has been shown to affect the properties of the gel formed.

The important connection between the fall in free peroxide content and the rise in viscosity, previously described, was only characteristic



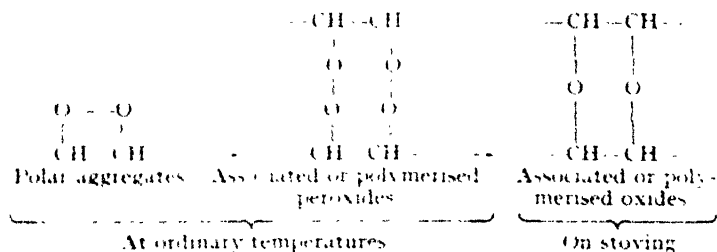
of the association process when taking place in a polar solvent. Those gels, which were rapidly precipitated from non-polar solvents such as carbon tetra-chloride and benzene, gave a theoretical figure for one peroxide grouping at each of the "remote" chain ethenoid linkages and showed no such fall. It was clear, therefore, that the peroxide radicals in these rapidly formed gels were not combined in the same manner as those in the polymer- produced in polar solvents, and remained comparatively free. It is possible that in the complexes produced slowly in polar solvents, molecule is linked to molecule by primary valency forces operating at the peroxide radicals, such a combination not being broken down by the reagents used for estimating the free peroxide content, but later experiments have provided another explanation. Those gels, however, produced rapidly in non-polar solvents and precipitated as such, are of the character of molecular aggregations

in which polar forces or secondary valencies are the binding influence. The full complement of peroxide is given as a result of degradation of this polar aggregation by the reagents used in the peroxide estimation.

It is as yet too early to characterise in detail the nature of these secondary valencies, but evidence is accumulating from many sources to establish their importance in all types of resinification of which the drying oils and synthetic resins are but two classes.

Transition from polar aggregation to the true polymeric state is not effected easily at ordinary temperatures so far as the gels from the β maleic anhydride compounds are concerned, a characteristic indicated by the polar aggregations retaining their complement of free peroxide unchanged for 12 months.

Two series of observations may throw light on this transition from polar aggregates to true polymers. In the first series, the peroxidic polar aggregate from carbon tetrachloride was heated with glacial acetic acid at 100–110° C. for several hours. From the solution a brown amorphous substance was obtained whose peroxide value had fallen from 3.59 per cent. to 0.8 per cent. and on analysis showed a marked increase in the percentage of carbon. In the second series the same pale yellow gel was heated alone at 110° C. for six hours in an inert atmosphere after which the peroxide value had fallen to 0.39 per cent. Analysis of the brown gel gave a rise in carbon percentage which corresponded quantitatively to the loss of peroxide oxygen. The conclusion drawn is that on stoving a peroxide film of a drying oil, loss of active oxygen ensues and there is a linkage of molecules of the glyceride through the remaining oxygen atoms to form condensation polymers. The arrangement of these chains is as yet unknown. This association is of a different type to what occurs when a drying oil film sets at ordinary temperature to give peroxides, and may represent the character of such a film on stoving.



The slow fall in the peroxide value and the corresponding rise in viscosity as given in Fig. 1 may indicate that gradual decomposition of the peroxide occurs in glacial acetic acid, and associated oxides, possibly of a chain character are formed with an increase in viscosity of the solution. This aspect seems more probable than to put forward that chain polymers of peroxides are formed. This explanation would account for the improved durability of stoved films and for the gradual disappearance of "bloom," which has been shown to be dependent on the presence of peroxides.⁴

At ordinary temperatures the disappearance of the peroxide is very slow, and even at 100°–110° in glacial acetic acid is not complete after several hours' heating.

These results explain the difference in the drying time of the maleic anhydride compounds of α and β elæostearin, and it seems clear that

⁴ N. K. Adam and Morrell, *J.S.C.I.*, 1934, **53**, 255T.

in the drying of an unsaturated oil the position of the ethenoid linkages in the characteristic acid is of primary importance in deciding the speed with which a hard film is formed. Ethenoid linkages remote from a carboxyl radical oxidise to a peroxidic condition and in this form are responsible for the molecular association of the compound. Ethenoid linkages relatively near to the carboxyl radical oxidise to a non-peroxidic structure and do not contribute to the association in so far as ordinary temperatures are concerned.

It should be mentioned that the "remote" chain ethenoid linkage in the β compounds is by far the most active towards oxygen of any of the linkages in these compounds. B. Hughes⁵ has examined films of these maleic anhydride compounds by surface potential methods and has shown that the induced polarity of the double bond in the chain can be traced from the anhydride radical. This induced polarity accentuates the intrinsic polarity of this bond in the case of the β compounds and depresses it in the case of the α . Similarly the ring ethenoid linkages would be subject to the same influence, and the complete inactivity towards oxygen of the ring ethenoid linkage in the α compounds is explained thereby.

The chemical and physical investigations of these compounds are therefore in agreement.

Summary.

The combination of maleic anhydride and α and β elæostearic acids and their corresponding glycerides has been investigated further.⁶

(1) Examination of the atomic models of the eight possible isomeric forms of elæostearic acid and a consideration of their reaction with maleic anhydride would assign to the α elæostearic acid the arrangement of the three double linkages as T--C--C, and to the β elæostearic acid the form C--C--T.

(2) The oxidation of the maleic anhydride compounds of α and β elæostearic acids and their glycerides has been studied. The influence of polar and non-polar solvents on the molecular aggregation of oxidation products was noted, and especially the action of oxidation catalysts in those media.

Only in the case of β elæostearic maleic anhydride compounds were peroxides produced at the remote double linkages. In the case of the α compounds tautomeric keto-hydroxy compounds were formed and the ring double linkages were not attacked. In the case of the β compounds the ring double linkages were oxidised to the keto-hydroxy form. Association of the peroxide was shown to take place, but no association occurred in the case of the α compounds or in the ring double linkages of the β varieties.

(3) The association of the peroxides formed in non-polar solutions is that of molar-aggregates due to the potential of the remote double linkage together with the addition of the strongly polar peroxide group.

In the polar solvents β compounds show association due to combination of primary valencies from the peroxide groups as indicated by the increase in the viscosity of the solution corresponding to a fall in peroxide value.

(4) The character of the associated "oxyns" has been investigated, especially the action of solvents on the associated "oxyns" and their behaviour on heating.

⁵ *J.C.S.*, 1933, 338.

⁶ Morrell and Samuels, *J.C.S.*, 1932, 2251; Morrell, Marks and Samuels, *J.S.C.I.*, 1933, 52, 130T.

It has been found that the peroxide oxyn formed at ordinary temperatures undergoes decomposition with loss of peroxide oxygen when heated either alone at 110°C . or in glacial acetic acid at the same temperature, indicating the formation of peroxide free condensation products. An explanation of the changes occurring during the stoving of drying oil films is advanced. It is probable that the slow fall in peroxide value accompanied by increase in viscosity in polar solvents is due to gradual decomposition of peroxide aggregates to give chain-like polymers of oxides; this would account for changes occurring in the ageing of drying oil films and in the disappearance of "bloom," which is ascribed to the presence of free peroxide groups.

(5) In view of the fact that the properties of the β elæostearin maleic anhydride compound are so similar to those of oil varnishes, especially Tung oil, and that it is possible to obtain these compounds in a pure form, it is hoped that many of the difficulties in investigating drying oil systems may be overcome. The results given in this and earlier communications favour such anticipations. The study of the oxidation has shown that the rate of oxidation as well as the character of the product are closely connected with the structure of the oil and especially with the position of the double linkages in its constituent glycerides.

(6) Of special interest is the observation of Hughes on the marked difference between the surface potentials of the α and β maleic anhydride compounds, which shows how the polarity of the double linkages have increased or decreased by the attachment of the anhydride group.

(7) The valuable collaboration of Professor Rideal and Mr. Gee by their use of strictly physical methods has given results which correlate chemical and physical methods, so that the conclusions acquire a strength which either method alone would fail to obtain.

The study of the maleic anhydride compounds of other drying oils and their acids is in progress and it is hoped that further collaboration of chemical and physical methods will be possible.

The authors wish to thank the Government Grant Committee of the Royal Society and Messrs. Imperial Chemical Industries Ltd. for grants in aid of the research, and Professor W. N. Haworth, F.R.S., and the University of Birmingham, for providing facilities for carrying out the work.

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GENERAL DISCUSSION.

Dr. N. K. Adam (London) said: The evidence actually given by Mr. Gee in this paper seems to me insufficient to justify the view that the large increases in area which he has followed in detail are due to polymerisation, or combination between adjacent molecules in the film. It is evident that a rather complex reaction is occurring, but I suggest that, although polymerisation may be the cause of the gel-like elasticity observed in the final films, it is really oxidation which gives rise to the increase in area. My reasons for suggesting this are mainly that in all other known cases where oxidation of an unsaturated group in a hydrocarbon chain occurs at a point remote from the end group which forms the main anchorage to the water, the molecules tilt over at a greater angle to the vertical, thus occupying a larger area on the surface. It is not easy to see how mere combination between adjacent molecules would produce this increase of tilt and a larger area. The inhibitory action of hydroquinone on the increase of area seems to me most easily explained on the assumption that

it inhibits oxidation, not polymerisation. It may be, and probably is, the case that oxidation, once it has reached a certain stage, assists the polymerisation, but I would like to see much more evidence that the various reactions mentioned in the scheme at the beginning of the paper can be distinguished and studied separately. Perhaps Mr. Gee is in a position to give us some of this now.

Professor K. H. Meyer (*Genthod-Geneve*) said: It is well known that traces of superoxides accelerate the polymerisation of unsaturated compounds. Consequently any antioxidant such as hydroquinone which prevents the formation of superoxides inhibits also polymerisation.

Mr. G. Gee (*Cambridge*), in reply to Dr. Adam, said: The suggestion that the experimental results can all be interpreted on the basis of a series of oxidation processes is one which has already been carefully considered; but the conclusion which was reached is that no such mechanism is capable of giving an adequate account of the observations. There is, furthermore no *a priori* difficulty about the conception of a two-dimensional polymerisation process, and it is significant that Morrell and Davis working independently and by purely chemical methods on the bulk oxidation of the same material have arrived at a mechanism which does not differ significantly from the one presented here. A detailed account of the experiments is to be published shortly, but the evidence that we have to deal with true polymerisation processes may be summarised briefly here.

(i) The results of a very large number of reaction velocity determinations, showing excellent experimental agreement, demonstrate that the two processes identified as oxidation and polymerisation stages are entirely different kinetically; the effect of pressure on these two reactions is in the opposite sense, the oxidation being retarded and the polymerisation accelerated by rise of pressure. These observations are in complete accord with the retardation of surface oxidation by pressure found by Hughes and Rideal; and with the well-known accelerating influence of pressure on polymerisation in the bulk phase.

(ii) The effect of diluting the film with various esters—ethyl myristate, methyl linoleate, ethyl linolenate, and methyl β -elaeostearate—is difficult to understand on any basis other than the one given in the text. The film is not collapsed, and its area and potential (corrected for the contribution of the ester) are practically unchanged by the dilution. Furthermore, a simple change in orientation would be revealed by a change in the *oxidation rate*—this is not observed.

(iii) The observed area changes show that considerable molecular re-orientation must be involved. Now since the compression of the molecule under the conditions required for polymerisation is such that the double bond is already located in the surface, it is impossible to see how any major area changes could result from a simple oxidation. Study of a molecular model reveals that the formation of oxygen bridges between the oxidised double bonds—which are located immediately above the double ring systems formed by the maleic anhydride residues—must cause the molecules to incline outwards from the point of attachment. This distortion will necessarily result in the molecules occupying a larger area on the surface; and the expansion will increase rapidly with the growth of the polymer. This factor is probably important also in restricting the size of polymer which can be formed. It may be noted, in support of this view, that β -elaeostearin does not show these large expansions.

(iv) The physical characteristics of the final film are admitted by Dr. Adam to suggest the presence of polymers. It should be emphasised that the production of these viscous films is so intimately bound up with the extent of the expansion that one can only conclude that the area change is actually produced by the polymerisation.

(v) The inhibitory effect of hydroquinone is not surprising, as antioxidants are frequently inhibitors for polymerisation also; the mechanism of catalysed and inhibited polymerisation is as yet imperfectly

understood, and the fact that hydroquinone inhibits a reaction is no sufficient criterion on which to decide whether the reaction in question is oxidation or polymerisation.

Dr. N. K. Adam (*London*), in reply to discussion with Professor Kurt Meyer, *communicated*: The fact that hydroquinone sometimes inhibits polymerisation in bulk does not prove that the area increases in the monomolecular films are due to polymerisation; after all, the commonest action of hydroquinone is to inhibit oxidations. Further, is it not likely that, where hydroquinone inhibits polymerisation, it does so because it inhibits the formation of those oxidised compounds which so often seem to act as catalysts for the polymerisation of unsaturated compounds, *i.e.*, that even in these cases, its action is essentially anti-oxidative? It may perhaps be very difficult to separate oxidation from polymerisation reactions in these drying oils; but the importance of doing so, if possible, is very great. I am very glad that Mr. Gee is following the course of these reactions in the monomolecular films, where the orientation of the molecules can easily be determined; but I am anxious to see more convincing proof that the changes in area are really due to polymerisation instead of to oxidation, for oxidation would appear the simpler explanation of area increases, from what is known already about the behaviour of surface films of long chain fatty compounds.

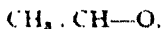
Dr. N. K. Adam (*after further communication*): I am much obliged to Mr. Gee for clarifying the evidence, and also for being good enough to show me some of the surface pressure-area curves on the material in the various stages from unoxidised to oxidised and polymerised. These curves afford strong additional evidence for his theory; the "fully polymerised" curve is that of a coherent film at low pressures, while that of the "stable isomer" of the unpolymersed oxidised film is apparently gaseous at low pressures; at higher pressures the curves cross and it is clear that there would be an increase in area, measured at medium and high compressions, accompanying the polymerisation. May I say that I now think he has made out an excellent case for his scheme of reactions.

Dr. J. H. de Boer (*Lindhoben*) said: Perhaps it may be possible that the unstable peroxide XO_2^* does not change into the stable one when it is absolutely dry. This leads to the following suggestion. Should it be possible to oxidise the molecules X to XO_2^* when spread on a clean metal surface (*e.g.* obtained by sublimation *in vacuo*) in a dry atmosphere, then afterwards this surface might be rinsed with dilute sulphuric acid to spread the XO_2^* on this liquid and perhaps so the polymerisation of XO_2^* could be studied apart.

Dr. E. Bergmann (*Rehoboth*) said: The suggested reaction scheme reminds one very much of the mechanism proposed by Bodenstein for the oxidation of acetaldehyde, acetylene and similar compounds. An unstable peroxide XO_2^* is formed, *e.g.*, $\text{CH}_3 \cdot \text{CH}=\text{O}$, which by reaction with a



second molecule X (*i.e.*, acetaldehyde) gives a stable peroxide XO_2 (*i.e.*, peracetic acid) and an "active" molecule X^* which has been designed a



In our case, the active molecule X^* stabilises by polymerisation. The parallelism is rather striking. It may be added that even in the most common case of the autoxidation of benzaldehyde there are two known substances XO_2 ; in addition to the "normal" product, perbenzoic acid, a preliminary compound, which is the real carrier of the autoxidation process. The latter accounts for the transmission of half of the oxygen atoms taken up on to other aldehyde molecules—and may stabilise into perbenzoic acid by a side-reaction of the autoxidation process.

Dr. R. Spence (*Leeds*) said: The results which we have obtained at Leeds⁷ appear to be in agreement with the theory propounded by Norrish and Carruthers. In addition to the carboxylic acid catalysts studied by them, we have found that rapid polymerisation occurs when the walls of the reaction bulb are moistened with sulphuric acid. An attempt was also made to determine the nature of the equilibrium between solid and gas. Some of the polymer prepared at room temperature was heated up in the presence of the monomeric gas and a stationary condition was attained at 80°, when polymerisation and depolymerisation became equal. The nature of the gaseous product of depolymerisation has not yet been studied, but it is interesting to note that Auerbach⁸ has found the vapours of certain polyoxymethylenes to consist of molecules of the type $(CH_2O)_n$, where n may be as large as 8. However, when the room temperature polymeride was maintained at 80° for 17 hours, the rate of depolymerisation became extremely small. This is probably due to condensation of the end groups and the formation of longer chains or to the closer packing of existing chains, perhaps by cross linkages of the peroxide type. The chain mechanism of polymerisation advocated by Norrish and Carruthers is supported by other observations. Chlorine and formaldehyde react to give HCl and CO. If the proportion of formaldehyde is greatly increased, rapid polymerisation occurs.⁹ Reference may also be made in this connection to Lenher's observation¹⁰ that the presence of one per cent. of oxygen in ethylene at 500° greatly accelerates the rate of polymerisation, although in this case more than one molecule of polymeride results from a single reaction chain.

Dr. G. Gee (*Cambridge*) said, *in reply to Dr. de Boer*: The technique of spreading monolayers on metals has scarcely been sufficiently developed for this method of obtaining a pure peroxide film to be immediately practicable. It is, however, hoped at some future date to investigate reactions in monolayers on metallic substrates.

In reply to a question asked by Dr. Kienle: The experiments have been carried out in the main on $N/10$ or $N/100$ acid; water is to be avoided on account of its variable p_H , while the use of alkali introduces difficulties in avoiding contamination, and might lead to hydrolysis of the glyceride. The possibility of using the method for the evaluation of antioxidants is very attractive, and experiments on these lines have already been carried out: this work is now being extended and it is hoped to publish the results shortly.

Dr. R. C. W. Norrish (*Cambridge*) said: *In reply to Professor Mark*, I must state that we have not yet investigated the absolute values of the steric factors and the activation energy of the process. The matter is complicated by the fact that the reaction occurs at the cold surface, so that it is difficult to assess the number of collisions made by the gaseous monomeric form with the reactive points of the growing chain. Experiments over a wider range of temperature are, however, planned, and it is hoped that it will prove possible to obtain at least a partial insight into these matters.

We have not yet studied the effect of gaseous alkaline substances on the polymerisation of formaldehyde.

In reply to Dr. Spence, I should like to say that his observations of the depolymerisation equilibrium of the freshly formed solid polymer with the monomeric formaldehyde at 70° C. is especially interesting, and is in full accord with the curves shown in Fig. 8 on our paper. The fact that on keeping the polymer overnight no such equilibrium was observed suggests that there is a change in the structure of the polymer on standing, and it

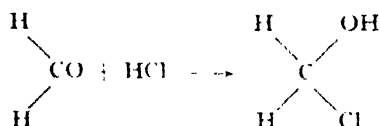
⁷ Spence, *J. Chem. Soc.*, 1933, 1103; Spence and Wild, *ibid.*, 1935, 338, 506.

⁸ Auerbach, *Arch. Kais. Gesundh.*, 1907, **22**, 584; 1907, **27**, 183; 1914, **47**, 110.

⁹ Spence and Wild, *J. Amer. Chem. Soc.*, 1935, **57**, 1145.

¹⁰ Lenher, *ibid.*, 1931, **53**, 3756.

will be interesting to compare the chemical properties of the two forms. He refers to the polymerisation induced by the reaction between chlorine and formaldehyde. This could be effected by the hydrogen chlorided produced which by addition to the monomeric formaldehyde would produce a hydroxyl group from which the Staudinger chains could grow.



We tried the effect of HCl on the polymerisation of formaldehyde, but though it was positive, it was small and no greater than that of water vapour. (See curve in Fig. 11 of our paper.) This is readily understood when it is seen that according to our mechanism, though both of these bodies can give rise to chains, neither can cause branching, and it is this latter factor which accounts for the enormously greater effects of formic and acetic acids.

MAGNETISM AND POLYMERISATION.

BY JOHN FARQUHARSON.

Received 4th July, 1935.

I. Introduction.

Although magnetic research has been used to show that a paramagnetic molecule may polymerise to form a diamagnetic complex, and measurements have been made on such systems in order to determine whether the molecule is single or more complex, it is remarkable that very little use has been made of the change in magnetic susceptibility when diamagnetic molecules polymerise. Recently Cabrera and Fahlenbrach¹ have shown that there is a depolymerisation of water resulting from the solution of salts, also it has been recognised that the change in the susceptibility of water with temperature results from a depolymerisation effect. It is the purpose of this paper to draw attention to the fact that magnetic measurements in purely diamagnetic systems can be used to follow the course of a polymerisation, and, in favourable circumstances, may be used to calculate the degree of polymerisation, i.e. the molecular weight of the complex.

II. The Additivity of Magnetic Susceptibility.

(1) Pascal's Work.

The exhaustive researches of Pascal² into the susceptibility of both inorganic and organic compounds have shown that magnetic susceptibility may be treated as an additive property. Pascal was able to deduce magnetic constants for atoms in combination in different molecules, but in order to predict correctly the susceptibility of molecules it was necessary to introduce certain constitutive values depending on the types of chemical linkages within the molecule.

¹ Cabrera and Fahlenbrach, *Z. Physik*, 1933, **85**, 568.

² For references, recalculation and discussion see Stoner, "Magnetism and Matter," pp. 469-474.

Pascal gave the expression for molecular susceptibility

$$\chi_M = \sum nA\chi_A + \lambda$$

where nA is the number of atoms in the molecule of susceptibility χ_A and λ is the constitutive constant depending on the chemical links.

(2) The Change in Magnetic Susceptibility Resulting from a Chemical Reaction.

The author³ has shown on purely experimental evidence that in simple addition reactions there is a change in magnetic susceptibility

TABLE I.—CHANGE OF MAGNETIC SUSCEPTIBILITY IN ADDITION REACTIONS.

Reaction.	Change in Molecular Diamagnetism.
$\text{NH}_3 + \text{HCl} \rightarrow \text{NH}_4\text{Cl}$	Fall 4.39
$\text{NH}_3 + \text{HBr} \rightarrow \text{NH}_4\text{Br}$	Fall 1.79
$\text{NH}_3 + \text{HI} \rightarrow \text{NH}_4\text{I}$	Rise 3.14
$\text{H}_2\text{O} + \text{SO}_2 \rightarrow \text{H}_2\text{SO}_4$	Fall 2.50
$\text{H}_2\text{SO}_4 + \text{K}_2\text{SO}_4 \rightarrow 2\text{KHSO}_4$	Fall 4.50
$\text{CH}_3\text{NH}_2 + \text{HCl} \rightarrow \text{CH}_3 \cdot \text{NH}_2 \cdot \text{HCl}$	Fall 4.47

consequent on the formation of a new chemical link, and that this change is usually in the direction of a fall in molecular susceptibility as shown in Table I.

That this change is a fall in diamagnetism is not necessarily correct because it will depend largely on the type of chemical link.

If, in an organic reaction, it involves the change from a —C=C— double bond to two single bonds, then according to Pascal's values there will be a rise in diamagnetic susceptibility of 5.5×10^{-6} .

III. Magnetic Changes during Polymerisation.

When polymerisation takes place between two molecules, B, to form a new molecule, the magnetic susceptibility of the new molecule will be given by an expression of the same type as that given by Pascal for the formation of a molecule from atoms namely,

$$\chi_M = 2\chi_B + \lambda$$

where χ_B is the molecular susceptibility of the molecule B, and λ is the constitutive factor arising from the new chemical bond. If n molecules B react to form a polymer nB , the general expression for the molecular susceptibility of the polymer will be

$$\chi_M = n\chi_B + (n - 1)\lambda$$

and the curve given by plotting χ_M against n will be a straight line. The mass susceptibility of the complex will be given by the expression

$$\chi = \frac{n\chi_B + (n - 1)\lambda}{nM_B},$$

where M_B is the molecular weight of the simple molecule B. In this expression χ_B , M_B and λ are constants and the curve for the change in mass susceptibility with the number of simple molecules in the complex will be a hyperbola. λ is given by Pascal's results so that by measuring χ , the mass susceptibility, it should be possible to calculate n . If n is small then it should be given with a fair degree of accuracy, but if it

³ Farquharson, *Phil. Mag.*, 1932, 14, 1003.

is large it will be rather uncertain. It will always be possible to give a lower limit for n and thus for the molecular weight. Also, it should be possible to follow the course of a polymerisation process.

IV. Following the Course of a Polymerisation.

If a polymerisation proceeds straightforwardly then the susceptibility plotted against time should give a hyperbola such as that for 2, 3-dimethylbutadiene in the Figure.

In the majority of the methods used for the measurement of magnetic susceptibility, it is the volume susceptibility, K , which is measured and the mass susceptibility then found by the relation $\chi = K/\rho$ where ρ is the density. If the mass susceptibility is increasing as the polymerisation proceeds, which is usual as the polymerisation often involves the disappearance of one or more double bonds, the increase in volume susceptibility will be even more marked, because in these polymerisation processes the density also increases greatly.

It is very easy to follow the change in susceptibility as the polymerisation proceeds by means of the Gouy method where the susceptibility is found from the force on a cylindrically shaped specimen suspended with one end between the pole pieces of the electro magnet where the field is uniform, and the other end where the field is negligible. If K_1 and K_2 are the volume susceptibilities of the specimen and the medium in which it is suspended, A the cross section of the specimen, and H the field, then the force on the specimen is given by

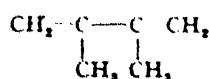
$$F = \frac{1}{2} (K_1 - K_2) AH^2$$

The force is easily measured by suspending the specimen from one arm of a sensitive weighing balance and is given by the difference in weight with and without the field. F then gives a direct measure of the volume susceptibility.

In actual practice where a liquid is being polymerised by heat, the specimen is placed in a uniform glass tube of cross section about 0.5 sq. cm., which is then drawn off into the form of a hook to allow of easy suspension. The tube may be previously standardised as to cross section and susceptibility. It is important that the column of liquid is sufficiently long to ensure that after polymerisation and resultant shrinkage the upper end of the column is still in a position of negligible field.

By using a sealed tube it is also possible to obtain an estimate of the density. The weight remains constant and by cooling the specimen to some standard temperature each time a measurement is made, and measuring the length of the column of liquid, it is possible to calculate the density. Should the final product of polymerisation be a solid, care must be taken to see that shrinkage does not leave a space between the solid and the walls of the containing tube and so alter the cross section. As a rule it is not necessary to measure the density during the polymerisation as it is the mass susceptibilities of only the initial and final states which are required.

V. The Change in Susceptibility of 2, 3-dimethylbutadiene as it Polymerises at 146° C.



The dimethylbutadiene was prepared from freshly distilled pinacone by heating with potassium pyrosulphate. The fraction containing the dimethylbutadiene was dried over calcium chloride, distilled, and finally distilled over sodium.

The measurements were made by the Gouy method just described. The polymerisation was done at 146°C . Before each measurement the tube was removed from the heating furnace and cooled to room temperature. The alternate heating and measuring were continued for some days

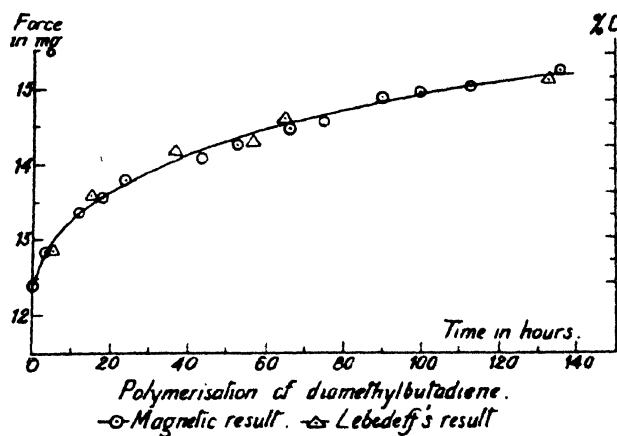


FIG. 1.

until the polymerisation was judged to be complete, the dimethylbutadiene having become quite viscous. The results are shown in the first and second columns of Table II, and in Fig. 1. The results are given as the force in milligrams

on the specimen in the magnetic field.

For comparison with the magnetic result, some results by Lebedeff⁴ are given in columns three and four of the Table and also in the Figure. Lebedeff estimated the amount of unchanged material after different times of heating at 150°C . It will be noticed that there is a change of about 2 per cent. in the volume susceptibility and that the susceptibility increases steadily with the time of polymerisation showing that the polymerisation proceeds steadily.

The density was not measured as the polymerisation proceeded, so the curve for the mass susceptibility cannot be given, but the mass susceptibilities of the initial and final products are,

Initial

$$\chi = -0.670 \cdot 10^{-6}$$

$$\rho = 0.730$$

Final

$$\chi = -0.7305 \cdot 10^{-6}$$

$$\rho = 0.823$$

TABLE II.—THE POLYMERISATION OF 2, 3-DIMETHYLBUTADIENE.

Magnetic Result, 146°C .		Lebedeff's Result, 150°C .	
Hours.	Millegram Force on Specimen.	Hours.	Per Cent. Changed.
0	12.38	5	15.1
3.25	12.84	15.5	38.4
12.25	13.37	15.5	41.0
18.25	13.54	30.5	59.4
23.8	13.80	50.5	61.0
44.0	14.03	60.0	71.8
52.0	14.22	60.0	75.4
66.8	14.43	133	87.3
75.5	14.48	264	95.0
90	14.88		
100	14.94		
113	14.98		
137	15.23		

VI. The Polymerisation of Cyclopentadiene at Room Temperature.

Cyclopentadiene affords an example of a susceptibility-polymerisation curve which falls with increasing polymerisation. The substance was

⁴ Lebedeff, *J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1313.

allowed to polymerise at room temperature, and the mass susceptibility was measured at intervals on a Curie-Cheneveau magnetic balance. The author is indebted to Dr. Wasserman of this department for a sample of freshly distilled cyclopentadiene. The results are given in Table III.

According to Barratt and Burrage⁶ cyclopentadiene polymerises fairly rapidly at room temperature to dicyclopentadiene and a small proportion of higher polymerides, and any further polymerisation takes place slowly. The magnetic results are in agreement with this view, but the value -0.680×10^{-6} cannot be taken as that of the dimer because the sample was still liquid and contained unchanged cyclopentadiene.

TABLE III.—SUSCEPTIBILITY OF CYCLOPENTADIENE

Hours.	$-\chi \times 10^6$.
0	0.717
2	0.713
18	0.688
26	0.684
41.5	0.680

VII. Further Examples of Change of Susceptibility with Polymerisation.

(1) Cyanogen Chloride.

Cyanogen chloride was prepared by the method of Price and Green⁸ by the action of chlorine on HCN. It was purified by distillation over sodium bicarbonate and zinc oxide. The substance was redistilled immediately before measurements were made. Cyanogen chloride polymerises readily in the presence of a little HCl to give the white solid polymer cyanuric chloride. The results are as on table opposite. The change in susceptibility when three molecules of cyanogen chloride polymerise to form cyanuric chloride is $(3 \times 32.4 - 81)10^{-6} = 16.1 \times 10^{-6}$ or 16.5 per cent.

(2) Nitrosobenzene.

Nitrosobenzene is a white solid at room temperature. When molten or in solution it is green and thus falls into line with other nitroso compounds. The colour change has been taken as an indication that nitrosobenzene is polymerised in the solid state. Cryoscopic data support this view.⁷ In acetic acid the molecular weight is 112 (theory 107) indicating polymerisation, and in benzene 101.6 — 106.

Magnetic results for nitrosobenzene are given in Table IV.

No really reliable figure can be given for the susceptibility of nitrosobenzene in benzene because of its slight solubility, but all the measurements made showed it to be less diamagnetic than when molten. The measurement on the liquid was made

TABLE IV.—SUSCEPTIBILITY OF NITROSOBENZENE UNDER DIFFERING CONDITIONS.

State of Compound.	$-\chi \times 10^6$.
(1) Solid	0.563
(2) In acetic acid	0.531
(3) Molten	0.450
(4) In benzene	less diamagnetic than when molten

⁶ Barratt and Burrage, *J. Phys. Chem.*, 1933, **37**, 1029.

⁸ Price and Green, *J. Soc. Chem. Ind.*, 1920, p. 30.

⁷ Bamberger and Renaud, *Ber.*, 1897, **30**, 2278; Bamberger and Rising, *Ber.*, 1907, **34**, 3878.

at 72° C., which is only 2° above its melting-point. Higher temperatures for the time necessary to make a measurement gave rise to decomposition.

The magnetic results support the view that the solid nitrosobenzene is polymerised. It would appear that there is still a quantity of polymer in acetic acid and also a small amount in molten nitrosobenzene just above the melting-point.

Discussion.

Dimethylbutadiene.

According to Stoner's recalculations of Pascal's values for magnetic constitutive effects the values for λ for a double bond and a conjugated double bond respectively are

$$\begin{array}{ll} \text{---C=C---} & 5.5 \times 10^{-6} \\ \text{---C=C---C=C---} & 10.6 \times 10^{-6} \end{array}$$

Whitby and Crozier⁸ have shown that dimethylbutadiene which has been polymerised for fifteen days at 150° contains 63 per cent. of a dimer and 37 per cent. of higher polymers. The higher polymers still contain one double bond per diene group as does the dimer because it is a ring compound, so that one double bond disappears for each addition of a dimethylbutadiene molecule. In this case the bond change λ will be 5.1 and the application of the formula

$$\chi = \frac{n\chi_B + (n-1)\lambda}{nM_B}$$

gives a value for $n = 36.4$ i.e., the mean molecular weight is 2985. On the other hand, if the bond change is simply looked upon as the disappearance of a double bond, $\lambda = 5.5$, and $n = 10$. The mean molecular weight is 820.

If the results of Lebedeff and Whitby are combined then the mixture of polymers measured magnetically should contain approximately

$$\left. \begin{array}{l} 12.1 \text{ per cent. of monomer} \\ 55.4 \text{ per cent. of dimer} \\ 32.5 \text{ per cent. higher polymers} \end{array} \right\} \text{mean molecular weight 750,}$$

but the percentage of higher polymers may be slightly higher and that of dimer lower, as after 12.5 hours heating at 145° C. the ratio of higher polymers to dimeric oil is higher. It appears from this that the bond change in a polymerisation process of this type is 5.5 and not 5.1. The agreement is very good but the result may not be reliable as Pascal's values cannot be regarded as precise, but are only average values, and for this type of work very reliable and accurate values are required for the bond changes involved. This result for dimethylbutadiene can only be regarded as a preliminary one. A more accurate examination is being carried out on isoprene and its polymerisation products, for here, at least, some of the simpler polymerisation products are known in the form of the terpenes.

Cyclopentadiene.

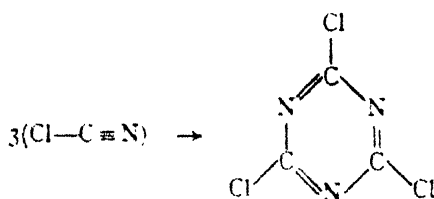
According to the accepted view of the polymeric cyclopentadienes the mass susceptibility of cyclopentadiene should rise as it polymerises,

⁸ Whitby and Crozier, *Canadian J. Research*, 1932, 6, 203.

as polymerisation results in the disappearance of two double bonds. Instead of a rise there is a fall which is difficult to explain unless there is a large fall in diamagnetism due to the bridged ring of the terminal six membered ring of the polymeric cyclopentadiene.

Cyanogen Chloride.

The value of 32.4 for ClCN is slightly higher than that given by Pascal's values, 30.8. This is only to be expected because although Pascal's atomic values give good results, it is the values of certain groupings which are more likely to give additive results than atomic values. However, it will be seen that the large change in diamagnetism when cyanogen chloride polymerises to cyanuric chloride can be explained readily by the use of Pascal's values. The commonly accepted view of the polymerisation is



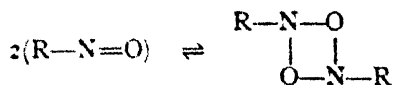
According to Pascal, the bond constitutive effects are



so that the disappearance of 3(C≡N) bonds should raise the susceptibility by 2.4 and the appearance of 3(C=N) bonds should lower it by 24.0, a net change of 22.2 whereas the change found experimentally is 16.1.

Nitrosobenzene.

The susceptibility of the nitroso compounds is slightly abnormal and will be treated more fully in another publication, but if the structure is formulated in the old way, then



The double bonds disappear from between the oxygen and the nitrogen which would make the polymer more diamagnetic than the monomer as is found experimentally.

Summary.

Polymerisation gives rise to a change in diamagnetic susceptibility which can be followed quite easily. As polymerisation proceeds, the mass susceptibility follows a curve which, in the normal case, is a hyperbola. If the degree of polymerisation is not too great then it can be calculated by using Pascal's atomic values or constitutive constants. Pascal's values can also be used to explain the changes in susceptibility when the polymers can be separated.

The author expresses his thanks to Professor F. G. Donnan for his continued interest and advice, to the Commissioners for the Exhibition of 1851 for a Senior Studentship with which this work was begun, and to Imperial Chemical Industries for a Grant.

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GENERAL DISCUSSION.

Dr. R. J. W. Le Fèvre (*London*) said: Abnormalities in the case of nitrosobenzene are not unexpected, since a completely satisfactory formula—upon the basis of which such an additive property as magnetic susceptibility could be calculated—is lacking for this substance. Experimental evidence showing that monomeric nitrosobenzene cannot be regarded as containing a tercovalent N atom (as required by the older formula) has been cited previously (Le Fèvre),⁹ whilst from a consideration of the variable and at first sight contradictory electropolar properties of the nitroso group in aromatic compounds (polarisation¹⁰ and polarisability¹¹ effects), the conclusion was reached¹² that Ar-nitroso compounds must be formulated uniquely. To this end a suggestion was advanced that these phenomena would be understandable if the NO radical were to exhibit degeneracy to a certain degree between the unperturbed forms $-\text{N}^{\cdot}(\text{O})$ and $-\text{N}^{\cdot+}-\text{O}^{\cdot-}$. Expressed in a current nomenclature,¹³ it can be said that an Ar-NO group is to be classified as having superposed polarisations of $-I$ and $-M$ types along with polarisability possibilities denoted by $\pm E$.

⁹ *J.C.S.*, 1932, 2503.

¹² *Nature*, 1932, 400.

¹⁰ *Ibid.*, 1932, 2239.

¹¹ *Ibid.*, 1931, 810.

¹³ Ingold, *J.C.S.*, 1933, 1120.

PART II.—SPECIAL.

RECENT PROGRESS IN THERMAL POLYMERISATION AND CONDENSATION OF GASEOUS HYDROCARBONS.

BY A. E. DUNSTAN.

Received 3rd September, 1935.

In a recent communication¹ "Thermal Treatment of Gaseous Hydrocarbons—(1) Laboratory Scale Operation," attention was drawn to the possibility of utilising gaseous hydrocarbons, such as natural gases, and gases from oil-cracking plants, as sources of motor fuel of high anti-knock value.

From the industrial viewpoint, the production of liquid hydrocarbons from gaseous paraffins and olefines is of great importance owing to the vast quantities of these hydrocarbons available for development.

The quantities of gaseous olefines available are more difficult to estimate because of the considerable variation in the gases produced in cracking operations. A figure of 300,000 million cu. ft. may be taken as the volume of cracker gas produced in a year, and of this it is estimated that the quantities of gaseous olefine hydrocarbons available from this source, expressed in millions of cu. ft. are: ethylene, 16,500; propylene, 2000; butylenes, 11,000.

Polymerisation of Olefines.

Historical references are given in two papers by Dunstan, Hague, and Wheeler.² Further, in these two papers is developed the general theory of the polymerisation of the simpler olefines as set out in the following paragraphs.

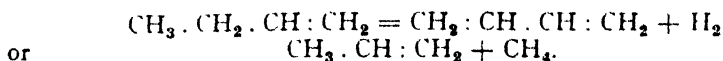
With the olefines, ethylene, propylene, and the two unbranched butylenes, the principal primary reactions, common to all, involve the formation of either the two-carbon or the four-carbon (or both) atom members of the olefine series. These reactions may be represented by: (i) $2C_2H_4 = C_4H_8$; (ii) $2C_3H_6 = C_2H_4 + C_4H_8$; (iii) $C_4H_8 = 2C_2H_4$. Whilst the exact mechanism of reactions (ii) and (iii) is obscure, it has been shown that reaction (i) is a true polymerisation.

If conditions are at all drastic, decomposition is not limited to the the primary changes, and secondary reactions occur, such as the

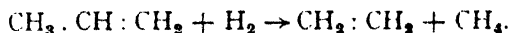
¹A. E. Dunstan, E. N. Hague, and R. V. Wheeler, *Ind. Eng. Chem.*, 1934, **26**, 307.

²*J.S.C.I.*, 1931, **50**, 313, and *J.S.C.I.*, 1932, **51**, 131.

decomposition of butylene to give butadiene and hydrogen in one case, and propylene and methane in the other:



An important secondary change with propylene is the formation of methane and ethylene, probably by hydrogenation of the radicals formed by scission of the carbon chain at the single linking, as shown by:



Of the two butylenes, it was found that Δ^{β} -butylene was more stable than Δ^{α} -butylene. Three changes appear to be operative to approximately the same extent at 600° : (i) Depolymerisation to ethylene, accompanied by the secondary hydrogenation of the ethylene to ethane. (ii) Scission of the carbon chain at the end single linking, with the formation of radicals which by hydrogenation give rise to propylene and methane. (iii) A dehydrogenation of butylene to form butadiene.

It has been shown that, following on the production of butylene from ethylene, secondary decomposition to give butadiene occurs. Furthermore, ethylene and butadiene combine in equimolecular proportion, at comparatively low temperatures, to produce cyclohexene. Thus it would appear that, following on the primary modes of decomposition, there is the production of hydroaromatic and then aromatic hydrocarbons. With both paraffins and olefines, ethylene would appear to be the starting-point for these changes. The experiments of Dunstan, Hague, and Wheeler show, then, that ethylene readily polymerises to butylene, that butylene by dehydrogenation produces butadiene, that butadiene and ethylene unite in equimolecular proportions to give cyclohexene, and that cyclohexene finally produces benzene.

The exact mechanism of the addition of ethylene to butadiene is not clear. There are indications that an open-chain hexadiene and then a cyclohexadiene may be intermediate steps in this change, but no satisfactory proof of this can be adduced as yet.

By analogy with the formation of diphenyl from benzene, it is

TABLE I—PYROLYSIS OF THE OLEFINES FOR THE PRODUCTION OF AROMATIC HYDROCARBONS AT ATMOSPHERIC PRESSURE

Gas.	Temp	Conversion into Liquids	Conversion into Light Spirit.
		Per Cent.	Per Cent.
Ethylene	800°	36.1	17.7
Propylene	750°	35.6	20.4
	800°	40.6	19.0
Δ^{α} -Butylene	700°	35.8	23.6
	750°	39.6	22.45
Δ^{β} -Butylene	700°	37.0	25.8
	750°	39.6	23.2

reasonable to suppose that butadiene can condense with benzene, hydrogen being eliminated, to form naphthalene, and that anthracene and phenanthrene can be formed from naphthalene in a similar manner. It is interesting to note that considerable quantities of styrene were found in the liquids obtained when operating on a

semi-large scale. The most obvious explanation of the presence of styrene is by condensation of ethylene and benzene, with the elimination of hydrogen.

The olefines, ethylene, propylene, and the branched butylenes, have

been considered individually in a pure state. As with the paraffin hydrocarbons, it was found that, following on the primary reactions brought about by heat-treatment, secondary reactions occur which lead to the production of aromatic hydrocarbons. This stage in the pyrolysis of the olefines closely resembles that observed with the paraffin hydrocarbons. Some of the figures obtained are given in Table I.

At lower temperatures, however, true polymerisation without these secondary changes occurs. Thus it is found that at all pressures from 200 to 2000 lb. per sq. in. over the temperature range 350° - 600° liquid hydrocarbons can be produced from ethylene. Neither 200 nor 2000 lb. per sq. in. is a limiting pressure for this effect, but this range has proved convenient. As the pressure is increased, the temperature necessary to effect polymerisation is reduced. Under suitable conditions it is possible to operate without the production of more than traces of saturated gases from the olefine hydrocarbons, but always, if conditions are too drastic, deposition of carbon accompanied by the production of hydrogen and saturated gaseous hydrocarbons occurs.

The liquid hydrocarbons from continuous operation possessed a light straw colour and were quite transparent. The boiling range of these liquids varied with the conditions of temperature and pressure of their production, but the usual product had a specific gravity of 0.75 to 0.77 at 15° C., and 80 to 86 per cent. distilled below 200° C. The liquid has been fractionated through an efficient fractionating column, and "steps" occur at 37° to 39° , 64° to 66° , 94° to 98° , 100° and 120° C. These steps, together with the evidence supplied by gas analysis, indicate the presence of olefines or paraffins, or both, containing from 3 to 8 carbon atoms to the molecule. Thus, from gas analyses, propylene, the butylenes and the amylenes are present. Furthermore, the percentage unsaturation of the liquid fractions has been estimated, and it has been found that this decreased with rise in temperature from 75 to 80 per cent. in the region of 39° C., to 50 per cent. in the 120° C. range. Thus the polymerides are largely olefinic, with an increasing proportion of paraffins as the boiling-point increases. All fractions were stable when exposed to sunlight, and gave no reaction with maleic anhydride. These facts are taken as evidence that hydrocarbons containing conjugated double bonds in the molecule were absent. There are, however, indications of the presence of naphthenes.

A brief account follows of work only published very recently or described in current meetings, particularly of the American Chemical Society in New York this spring.³

Cracking and Polymerisation of Low Molecular Weight Hydrocarbons.

Considerable interest has been shown lately in the polymerisation of gaseous olefines for the production of anti-knock fuels. The writers have already presented some results of a general nature on the subject.⁴

Polymerisation of Olefines.

At low temperatures, in the absence of catalysts, the olefines require a long time of heating to produce good yields of liquid products. At higher

³ By P. K. Frolich and P. J. Wiezevich, presented before the Petroleum Division, American Chemical Society, New York Meeting, April 22-23, 1935.

⁴ Frolich and Wiezevich, *Ind. Eng. Chem.*, 1932, **24**, 13.

temperatures the rate of polymerisation is much greater, but a different type of product is obtained.

Use of Catalysts with Olefines.

A large number of catalysts and contact materials have been reported for the polymerisation of olefines. Silicon, copper, and noble metals, boron fluoride, zinc chloride, boron fluoride with hydrogen halide, aluminum chloride with zinc and others have been shown to have high activity. By means of boron fluoride accompanied with finely divided nickel the polymerisation of ethylene may be controlled to give high yields of butylene.

Silica gel was found to catalyse the formation of aromatics from propylene at 650° C. Clay at 170° to 370° C. at 600 to 1500 lbs. pressure has also been found effective in polymerising gaseous olefines. Gayer prepared a synthetic alumina-silica catalyst which is more active in polymerising propylene at atmospheric pressure than Floridin clay, at 350° a 30 per cent. yield per pass of low boiling liquid products was obtained having a high octane number (87 after steam distillation) and boiling mostly in the hexane range.

Phosphoric acid and its salts have also been found effective in polymerising gaseous olefines. Ipatieff has employed orthophosphoric or orthophosphoric acids for polymerising cracked gases.

Other catalysts which have been employed for this purpose are basic zinc chromite, metals of the 8th series, ammonium molybdate, magnesium oxide and bauxite.

Polymerisation of Gaseous Olefines with Phosphoric Acid.

Part I. Catalytic Polymerisation of Propylene by means of Phosphoric Acid.⁵

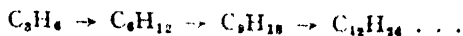
The polymerisation of olefines, both catalytic and non-catalytic, has received little study from the point of view of the chemical mechanism of the process.

Our explanation of the catalytic action of phosphoric acid is based on its ability to form esters with olefines. These esters, in turn, decompose to liberate activated olefine molecules which combine to form polymers.

Experiments have shown that olefines react with phosphoric acid at relatively low temperatures (200° C. for ethylene, 125° C. for propylene) to form esters of phosphoric acid.

At the temperatures employed in actual polymerisation the life of these esters is probably very short. The activated olefine molecules liberated *in statu nascendi* by the decomposition of these esters unite with each other to form polymers. Evidently, according to this hypothesis, a single molecule by phosphoric acid can bring about the polymerisation of many molecules of olefine since the acid is regenerated after each cycle. In one experiment on the polymerisation of propylene by liquid phosphoric acid, the quantity of polymer obtained corresponded to the polymerisation of 110 molecules of propylene by a single molecule of phosphoric acid, and at the end of the experiment the acid was as active as it was at the beginning.

The esters may eliminate the elements of phosphoric acid in different ways, thus giving rise to isomeric polymers. Thus the first formed hexylene may react with phosphoric acid to form hexyl phosphoric acid which in turn may react with propyl phosphoric acid to produce nonylene. In the same way nonyl phosphoric acid may react with propyl phosphoric acid to form dodecylene, or two molecules of hexyl phosphoric acid might produce dodecylene.

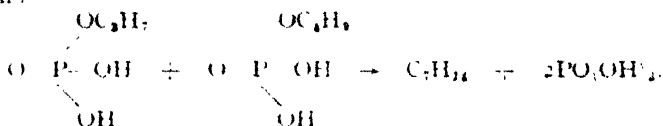


⁵ By V. N. Ipatieff, presented before the Petroleum Division, American Chemical Society, New York Meeting, April 22-23, 1935.

The polymerisation of propylene proceeds at high velocity at 200° C. under a pressure of 7 to 15 atmospheres. In fact it takes place readily at 135° C. at atmospheric pressure. The liquid polymer obtained by the polymerisation of propylene consists almost entirely of mono-olefins, C_nH_{2n} . The evidence for this statement as to the chemical nature of the polymer is four-fold: (1) solubility in 96 per cent. sulphuric acid at 0°; (2) behaviour on catalytic hydrogenation; (3) bromine number; and (4) carbon-hydrogen ratio. For example, the propylene polymer was practically 100 per cent. soluble in 96 per cent. sulphuric acid at 0° C. Catalytic Hydrogenation of the polymer at 220° and an initial hydrogen pressure of 96 atmospheres produced only paraffinic hydrocarbons which indicated the absence of naphthenes and aromatics in the original polymer. The bromine number of the polymer agreed with that calculated for mono-olefins, and the carbon-hydrogen ratio corresponded to C_nH_{2n} .

As mentioned above, the propylene polymer produced at the relatively low pressures of 1 to 15 atmospheres consists of mono-olefins, but under more severe polymerising conditions (higher pressures, temperatures and contact times), aromatic hydrocarbons are also formed. This is especially true in the catalytic polymerisation of ethylene.

In the polymerisation of a mixture of olefins, such as propylene and butylene, there is obtained not only the polymers of each of these hydrocarbons, but also mixed polymers due to combination of the two hydrocarbons. The evidence for this conclusion is Podbielniak distillation data of the liquid products obtained from individual olefins and from mixtures. The formation of a mixed polymer can be represented by the following equation.



Polymerisation of Propylene at Superatmospheric Pressure with "Solid Phosphoric Acid."

Many experiments were made on the polymerisation of propylene and of other olefins in the presence of so-called "solid phosphoric acid" catalysts. These contact masses were prepared by mixing phosphoric acid with various carriers. These solid catalysts, being non-corrosive in spite of their high acid content, could be used in ordinary steel apparatus. The catalytic activity depended to a considerable extent upon the method of preparation and upon the character of the solid absorbent.

Pursuing the same line of attack Ipatieff and Corson dealt with the butylenes.

Polymerisation of Gaseous Olefins with Phosphoric Acid. Part II. Catalytic Polymerisation of the Butylenes by means of Phosphoric Acid.⁶

The isomeric butylenes are polymerised by phosphoric acid at relatively low temperatures and atmospheric pressure to liquid polymers. These polymers are mono-olefins. Iso-butylene polymerises the most readily, and α -butylene the least. The presence of iso-butylene accelerates the polymerisation of the n -butylenes (but it is certain that *iso*-butene may be better handled as a source of *iso*-octane).

Special attention should be drawn in this connection to the reactions of isobutene. This hydrocarbon exists in the C_4 fraction of cracked gases

⁶ By V. N. Ipatieff and B. B. Corson, presented before the Petroleum Division, American Chemical Society, New York Meeting, April 22-23, 1935.

(and especially in high temperature cracking) and may be absorbed and polymerised by means of moderately concentrated sulphuric acid (probably via tertiary butyl alcohol and its degradation) into di-isobutene. This, of course, is readily reduced into iso-octane (the standard hydrocarbons for high anti-knock efficiency).

The Polymerisation of Propylene.⁷

Gayer's work⁸ on the polymerisation of olefines by acid catalysts was repeated with the purpose of ascertaining whether or not the five-, seven-, and eight- carbon olefines are actually formed.

The activity of the Gayer catalyst and the nature of the polymer were confirmed. Olefines not corresponding to multiples of the propylene molecule were clearly indicated in the distillation curves, and their presence definitely proved by the isolation and identification of certain individual hydrocarbons. Trimethylethylene composed the major portion of the pentene fraction, and evidence is presented that the seven- and eight- carbon groups contained 3-methylhexene-1 and 2, 3-dimethylhexene-2, respectively.

Examination of the dipropylene fraction demonstrated that it was composed primarily of two olefines, 2-methylpentene-2 and tetramethylethylene, and a saturated hydrocarbon, 2-methylpentane. Similarly, a mixture of heptanes, apparently 2-methylhexane and 2,3-dimethylpentane, were found in the next fraction. Small amounts of benzene and toluene were also almost certainly present in the mixture.

This remarkable variety of products might appear to be the result of cracking rather than polymerisation; yet further study showed that no gaseous products other than ptenenes were produced in the reaction. These results and the absence of any appreciable amount of product above C₁₁ are in sharp contrast to those obtained under milder conditions with more easily polymerised olefines such as isobutylene. The latter gives an apparently limitless series of hydrocarbons which, however, are multiples only of isobutylene.

Pyrolysis and Polymerisation of Gaseous Paraffins and Olefines.⁹

The exothermic character of the polymerisation reaction has been observed by many investigators in this field, in fact Waterman and Tulleners state that "ethylene at a temperature above 350° C. and under a pressure of 175 Kg./sq. cm. (ca. 175 atmospheres) decomposes with explosive violence."

The Productions of Gasoline by Polymerisation of Olefines.¹⁰

The C₄ fraction from the total gas yield was studied. Its approximate composition is 60 per cent. butene-1, 25 per cent. iso-butene, 13 per cent. 1,3-butadiene, and 2 per cent. a mixture of *n*-butane and isobutane.

From a survey based on the products obtained over the whole temperature range of thermal reactions of gaseous hydrocarbons, ethylene may be regarded as the basic hydrocarbon. The detailed nature of its thermal

⁷ Preliminary Paper, by Frank C. Whitmore and Robert F. Marschner, presented before the Petroleum Division, American Chemical Society, New York Meeting, April 22-23, 1935.

⁸ *Ind. Eng. Chem.*, 1933, **25**, 1122.

⁹ By F. W. Sullivan, Jr., R. F. Ruthruff, and W. E. Kuentzel, presented before the Petroleum Division, American Chemical Society, at New York, April 22, 1935.

¹⁰ By C. R. Wagner, presented before the Petroleum Division, American Chemical Society, New York Meeting, April 22-23, 1935.

reactions gives the key to the decomposition of any hydrocarbon since ethylene is an important product below 750° and since above 750° the products are essentially those of ethylene at that temperature.

By a consideration of five types of reactions for ethylene—(1) polymerisation, (2) hydrogenation to ethane, (3) scission of one C—H bond, (4) scission of the double bond and (5) dehydrogenation to acetylene—the reaction products may be accounted for. Determined or estimated values for the energy of activation for these reactions show inconsistencies arising chiefly from the assumption that ethylene is stable below 1000° .

Polymerisation of ethylene to non-aromatic liquids appears to take place by a combination of ethylene radicals or molecules. Experimental evidence does not support the formation of higher olefines by combination with methylene radicals.

The mechanism for the formation of aromatics from ethylene has not been definitely established. Since dehydrogenation of cyclohexane to give benzene does not occur to any appreciable extent without a catalyst, and since the formation of acetylene takes place largely at temperatures higher than the temperatures for the formation of aromatics, a combination of six methylene radicals with the expulsion of six hydrogens due to localised energy has been suggested as a possible source of aromatics.

Production of Gasolene by Polymerisation of Olefines.¹¹

Gases from low-pressure vapour phase cracking containing 20 to 24 per cent. of ethylene, 13 to 18 per cent. of propylene, and 6 to 10 per cent. of unsaturates in the four-carbon group were polymerised to liquid products by heat and pressure in the absence of catalysts.

On a once-through basis 1.7 gallons of gasolene per 1000 cu. ft. were obtained operating at 950° F. and 800 lbs. pressure; the yield was increased to 3.0 gallons by recirculating the gas derived from stabilising the liquid products. The yields were improved in a commercial unit to 3.25 gallons. By processing gas from stabilising vapour phase cracked distillates 9.0 gallons were obtained. By operating at low pressure and 1200° to 1300° F., the liquid products were mostly aromatic.

Polymer Gasoline from Cracked Gases.¹²

A commercial polymerisation unit recently put into operation is processing 3,000,000 cu. ft. a day of cracked gas, and producing about 5 gal. of polymer gasoline per 1000 cu. ft. This gasoline has an octane rating of 80–82 "motor method," and its blending value is higher than that of benzene or iso-octane.

The process is that developed by the Universal Oil Products Company, and reported at the recent New York meeting of the American Chemical Society.

The unit is operating under mild conditions of temperature and pressure, using a solid catalyst. The stabiliser gas being processed contains about 29 per cent. of propylene and butylenes.

Cracked gases are made up of paraffin hydrocarbons, and also members of the olefinic series—including ethylene, propylene, and butylenes. These olefines react at relatively low temperatures and pressures in the presence of the solid catalyst to produce polymer gasoline.

¹¹ By C. R. Wagner, *Ind. and Eng. Chem.*, August, 1935, p. 933.

¹² By V. N. Ipatieff and Gustav Egloff. Proceedings—Fifth Mid-Year Meeting American Petroleum Institute, Section III. Refining. Tulsa, Okla., 14–16th May, 1935.

Properties of Polymer Gasoline.

The outstanding characteristic of polymer gasoline is its high octane number and blending value.

Polymer gasoline has higher blending value than either benzene or iso-octane, although its straight octane value is lower—81 versus 97 and 100, respectively. Its blending value becomes higher the lower the octane number of the base fuel with which it is blended.

Reactivation of the Catalyst.

The solid catalyst gradually loses its activity with continued use, but it is readily regenerated with a controlled volume of air which burns off the highly polymerised, or carbonaceous material that deposits upon the catalyst. This reactivation step has been carried out a number of times; each time bringing the catalyst back to its original activity. The 22-day run reported in this paper was made with a catalyst which had been regenerated in the tower used for polymerisation.

Summary.

Experiments are described concerning the polymerisation of five samples of cracked gases in semi-commercial polymerisation units. The operating conditions of gas rate, temperature and pressure varied from 0.05 cu. ft. to 11.4 cu. ft. per hour per pound of catalyst, 450° to 500° F., and 100 to 175 lbs. per sq. in., gauge, pressure. The yields of liquid polymer ranged from 3.0 gal. to 8.4 gal. per 1000 cu. ft., with olefine polymerisations of 71 to 99 per cent.

GENERAL DISCUSSION.

Captain W. H. Cadman (*London*) said: Dr. Dunstan has outlined in his paper the main points of the experimental work conducted by the Anglo-Iranian Oil Company, leading to the successful polymerisation and condensation of gaseous hydrocarbons on a semi-commercial scale.

A petroleum cracking plant is an essential part of a modern oil refinery equipment, either as a means of increasing the yield of lighter fractions, such as petrol by cracking the heavier residues, or for reforming oils, which means improving the quality of lighter fractions by raising their anti-knock value. Whatever be the type of cracking plant in use, the production of a large quantity of gas is unavoidable, amounting in most cases to many millions of cubic feet per day. These cracked gases have a high olefine content, sometimes as high as 50 per cent. by volume.

It is with the application of polymerisation to these cracked gases that Dr. Dunstan's paper deals. He frankly admits that the exact mechanism of these operations is not yet clear. The discussion on polymerisation in all its aspects at this meeting has gone a considerable way towards helping us to understand the reactions involved. Some new light has been thrown on the problem, but much still remains hazy or unsolved, and will, I fear, not be completely clear until more work has been done on the kinetics of the polymerisation of these gaseous hydrocarbons.

The *Summary* of the paper might convey the idea that the polymerisation of such gases had only reached the semi-commercial operation stage. This is not so. In the paragraph dealing with "polymer gasoline from cracked gases" Dr. Dunstan mentions a commercial polymerisation unit, and I would like to say something more about this great achievement. In addition to the work carried out in this country, a great deal of pioneer work has been done in America, particularly by Dr. Egloff, Professor Ipatieff, and other chemists of Universal Oil Products Company, leading to the completely successful commercial operation stage. To-day a large-scale polymerisation plant treating 3,000,000 cubic feet of gas per day is in

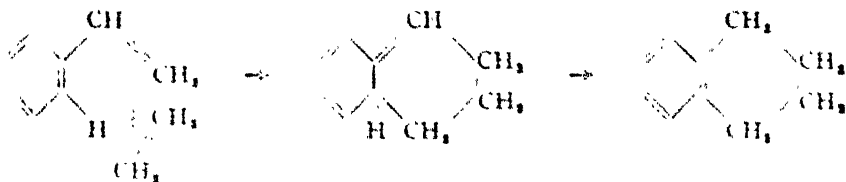
operation at the Shell Refinery in East Chicago, Illinois. There, the gas from the top of the pressure distillate stabiliser of the cracking point, at a pressure of about 150 lbs. per square inch is preheated to from 400° to 450° F. and then passed through several reaction vessels packed with phosphoric acid as catalyst supported on a suitable solid carrier. Half of these reactors are in use while the other half are being regenerated. The polymer product is a liquid of a light yellow colour. It is easily refined to a water-white motor spirit with an octane number of about 80. Dr. Dunstan has referred to the high quality of the polymer, and has pointed out that it is of greater value as a blending agent than benzene or iso-octane. So successful has this first commercial plant proved to be (yielding some 5 gallons of polymer gasoline per 1,000 cubic feet of cracked gas treated) that several other large-scale plants for the commercial polymerisation of olefines are now in course of construction in U.S.A. refineries.

The indications are that every modern refinery will soon find it desirable to add a standard "Poly" plant to their refinery equipment. Such plants are now on sale, and can be bought "over the counter" as it were, to deal with any number of millions of cubic feet of cracked gas per day, and with the yield and quality of polymer product fully guaranteed by the makers. Commercial gas polymerisation is one of the latest and one of the greatest developments in the oil industry. Its importance will be appreciated from the fact that it has opened up a new and valuable source of motor fuel supply.

I am sure, therefore, that all who are interested in the commercial application of polymerisation will join with me in congratulating the American chemists concerned on the translation of the polymerisation process into successful industrial production, and I would ask our American guests to convey these congratulations to their fellow countrymen on their return.

Dr. P. Lewis-Dale (*London*) said: Dr. Dunstan's paper deals with a practical application of polymerisation on a very large scale. It is singularly appropriate that it should be read at a meeting of this Society as Faraday himself in 1825 investigated a liquid obtained in the cracking of oil and found in it benzene and butylene. Armstrong (1884) worked on a similar liquid (from the Pintsch Oil Gas process) and isolated several compounds which polymerise readily. In 1924-25, I called attention to the fact that many substances in the liquid (obtained in the compression of oil gas) polymerised spontaneously or when treated with sulphuric acid and other reagents. When the liquid was distilled in glass, there was sometimes violent action at about 130° C., accompanied by evolution of hydrogen and polymerisation. The results noticed bear striking resemblance to some of the reactions mentioned by Dr. Dunstan. The liquid itself and distillates therefrom have very high anti-knock values, higher than that of benzene, which constitutes about 30 per cent. of the liquid.

Dr. E. Bergmann (*Rehoboth*) said: The suggested possibility, that naphthalene in the mixtures obtained is formed by interaction between benzene and butadiene, seems unlikely; the reaction should give phenylbutadiene. The following mechanism is preferred. Benzene reacts with ethylene to give styrene, hydrogen being eliminated. As a matter of fact, Dr. Dunstan has observed "considerable quantities" of styrene in his reaction products. A further molecule of ethylene now combines with the styrene according to the scheme.



subsequently, dehydrogenation occurs. The participation of the "conjugated" aromatic double bond in addition reactions of the above type has been observed in several cases: *e.g.*, in the reaction between styrene and diphenylketene, which, in variance with Staudinger's original view, is not a mutual saturation of the two olefinic double bonds of these molecules; in the reaction between asym. diphenylethylene and maleic anhydride (Wagner-Jauregg); in the formation of the so-called dimeric diphenyl ketone of Langenbeck, which is obviously not a cyclobutanedione-derivative, etc. A fuller report on these questions will be given elsewhere.

The formation of phenanthrene and anthracene from naphthalene may be explained according to the same reaction scheme.

ON THE FORMATION OF CONDENSATION PRODUCTS FROM SIMPLE HYDROCARBONS.

BY MORRIS W. TRAVERS.

Received 7th August, 1935.

The products formed by the thermal condensation of simple hydrocarbons are generally very complex, and a good deal of attention has been directed to the study of condensation processes by two methods. In the first place the methods of organic chemistry have been applied to the analysis of the products, conclusions as to the course of condensation processes being derived from the results; or the changes resulting in thermal treatment have been followed by observing changes of pressure. In the following paper an account is given of some experiments which lead to the conclusion that polymerisation may, in many cases be initiated by simple mechanisms, the nature of which can only be disclosed by detailed investigation. Such an investigation has been attempted in the case of ethylene, and also of propylene. A few experiments have been carried out in the case of acetylene, and the work done is sufficient to show that partial investigation of such a problem is more likely to prove confusing than helpful. I am a little doubtful whether the subject, as I treat it, comes within the scope of the discussion; but to deal with the general problems of polymerisation one must begin at the beginning, which is the study of the simplest hydrocarbons, ethylene and acetylene.

The difficulty in investigating condensation processes in the case of hydrocarbons, in common with the study of thermal changes in organic compounds generally, is partly due to the fact that two or more processes generally take place simultaneously, and only very exact analysis makes it possible to follow any single one of them accurately. Further, most processes seem to be more or less influenced by surface phenomena, which have either a positive or negative effect on the velocity of one of these which occur simultaneously. At the same time, the method of detailed analysis which we have used makes it necessary to confine our attention to a comparatively narrow range of temperatures; for at high temperatures the time during which the material is heated is so short that error due to the fact that the reaction tubes must be heated from air temperature to the reaction temperature becomes significant; and at low temperatures the processes become so slow that an investigation takes more time than can reasonably be devoted to it. Great accuracy

is also impossible when the processes are carried out under very low pressures.

In the whole of this investigation a method, which has been described in detail elsewhere, was used; a definite quantity of the reactant gas, or gases, being heated in a silica glass reaction tube to a definite temperature for a definite time, the contents of the tube being then analysed. The course of a reaction was followed by means of a series of such experiments covering different intervals, which made the method laborious. However, it was possible to trace the changes in concentration of each constituent or product exactly.

As it is impossible to follow the processes by means of formulae, methods of computation, of which the following is an example, were used. To determine the velocity constant in the case of the formation of condensation products, the rate of which is dependent on the square of the ethylene concentration, the amount of condensation product (R) produced during successive periods was divided by the product of the mean of the squares of the ethylene concentration at the beginning and end of the period, and the length of the period $K_v = \Delta R / (C_2H_4)^2 \cdot t$. The units used were concentrations in terms of gram atoms of carbon per litre, and hours.

The System Ethane: Ethylene-Hydrogen.

When pure ethane is heated to a temperature near to 600° it undergoes rapid primary decomposition into ethylene and hydrogen. The energy of activation of the process is about 75 K. Cal., so that, while at 600° equilibrium in the system ethane-ethylene-hydrogen is established almost instantaneously, at a little lower temperature there is considerable delay in the process. However, since on heating pure ethane there is a tendency to approach equilibrium with the products of primary decomposition, in studying the other thermal changes which occur when ethane is heated, over a range of temperature between 550° and 620°, it is convenient to use equilibrium mixtures of ethane, ethylene, and hydrogen, rather than pure ethane. Knowing the values of the equilibrium constants between the limits given above, any number of mixtures can be made up for any temperature, the limits of each series of mixtures being pure ethane on the one hand and pure ethylene on the other.

When Dr. L. E. Hockin and I commenced this investigation, in order to introduce some order into our work, we decided to investigate the properties of series of mixtures for which, in each series, the sum of the concentrations of $C_2H_6 + C_2H_4$ was constant, while the ratio C_2H_4 / C_2H_6 varied, the ratio, $C_2H_4 \times H_2 / C_2H_6$ remaining constant. The work was continued by Dr. T. J. P. Pearce and myself and a summary of the whole of the results was published¹ last year.

When ethane, or one of the equilibrium mixtures which contains a considerable amount of hydrogen, and does not approach very close to the ethylene end of the series, is heated to between 550° and 620°, methane and condensation products are formed. Study of a very wide range of mixtures had shown that there is no direct connection between the formation of methane and of condensate. However, it seems that ethane takes part only in the reaction involving its primary decomposition, and that both the condensate (R) and methane are derived, though by different processes, from ethylene.

We are not now concerned with the formation of methane, but reference must be made to the process by which it is formed. The rate of formation, in presence of hydrogen, appears to be proportional to the

¹ *J. Soc. Chem. Ind.*, 1934, **53**, 321-336T.

product of the concentration of the ethylene, and the sum of the concentrations of the ethane, methane, and hydrogen, activation resulting from collision of ethylene molecules with molecules of either of these species. Hydrogen concentration, at the higher temperatures, has some further effect on the rate of formation of methane. The addition of methane to an equilibrium mixture increases the rate of formation of methane from it, and the addition of other substances, such as silicon tetrafluoride has a similar effect.

For any series of equilibrium mixtures having the same total $C_2H_4 + C_2H_6$ content, though the ratio C_2H_4/C_2H_6 concentration varies considerably through the series, the rate of formation of condensate appears to be strictly proportional to the square of the ethylene concentration. The rate is not affected by the state of the surface of the reaction tube or by packing the reaction tube, at least at 590° , at which temperature the effect of surface was investigated. The effect of adding methane is negligible. However, when silicon tetrafluoride was added, the rate of formation of condensate was definitely increased.

Ignoring the fact last referred to, it would appear that the results point to a simple bimolecular process, on the assumption that the total carbon in the condensate produced represents the carbon derived from a primary process involving two molecules of ethylene. There was experimental evidence to prove that neither methane nor any three-carbon product was associated with the formation of the condensate.

However, while the rate of formation of condensate was constant for each series of equilibrium mixtures at constant $C_2H_4 + C_2H_6$ concentration, with fall in the total hydrocarbon concentration the value of the velocity constant tended also to fall, though the values obtained for very low hydrocarbon concentrations where the quantity of condensate was in any case very small, may be influenced by other factors, and need not be considered. Referring to Table I. in the paper by Dr. Pearce and myself, and taking as the mean values of K_p at any temperature and initial $C_2H_4 + C_2H_6$ concentration, the means of the value set down against the longest period for each series under index letter and number, (since the individual values of K_p are the mean values from time 0 to t), we have the following results:—

TABLE I.

Initial concentration $C_2H_4 + C_2H_6$	0.08	0.05	From graph, 0.05
620°	150.5	149	150
610°	139	130	118
590°	88	73	73
579°	—	40.5	43.5
550°	—	39	27

The values in the last column have been obtained by taking into consideration the fact that the data at 590° and 620° , in both cases with an initial concentration 0.05, are by far the most numerous and reliable, and plotting $\log K_p$ against $1/T$. The method can only give an approximate value for the critical increment of the process, which is found to be 35.5 K. Cal. It is slightly different from that adopted in the original paper, but the result is the same. It leads to the important conclusion that, if the process is assumed to originate in bimolecular

collisions of ethylene molecules, the number of effective collisions is only one in 10,000 of the number indicated by the simple calculation.

Pease² determined the rate of condensation of ethylene between 350° and 500°, using a copper vessel, and working at pressures between 2 and 9 atmospheres. Under these conditions the rate of formation of methane is very small. The formation of condensate was found to follow a *square law*, and from the temperature coefficient the critical increment was found to be 35 K. Cal. However, by extrapolation it is found that the rate calculated from his data at 590° is 7.5 times as great as the rate found in our experiments on equilibrium mixtures. We carried out a few experiments at 400° in silica apparatus, and while we found that it was difficult to obtain reproducible results, the rate was much less than that found by Pease. It is suggested that Pease's data are influenced by the effect of the copper surface. Pease notes that the rate calculated is 1000 times that found by experiment.

It may be noted that at low temperatures the product is a mixture of chain hydrocarbons, which, from an experiment which Dr. Hockin and I carried out, seem to contain not less than eight carbon atoms. Near 600°, as might be expected, the products are aromatic. However, it seems likely that the rate of formation of condensate is the rate of the primary bimolecular process, and that subsequent processes do not involve the separation either of methane or of 3-carbon compounds, so that the measure of the initial rate is the amount of carbon separating as condensate, in whatever form it may ultimately appear.

Before commencing work on the equilibrium mixtures, Dr. Hockin and I had investigated the thermal behaviour of ethane. We found very great difficulty in obtaining reproducible results, and came to the conclusion that this was due to the effect of oxygen, adsorbed on the walls of silica reaction tubes, or even passing through the walls of the tubes, when they were thin. The difficulty was overcome by filling the reaction tubes with hydrogen, and heating to about 600° for some hours before introducing the ethane. The difference between the behaviour of different tubes seems to depend upon the extent to which primary decomposition of ethane is catalysed by the surface.

When ethane is heated, primary decomposition sets in at once, and as both the condensate and methane are derived from ethylene, the velocity of formation of these products should be zero at the start, and should increase as the ethylene content of the gas increases. This is actually what takes place, and the graphs which represent the rates of formation of both products show accelerated velocities. However, if we neglect the short initial period during which the concentration of the ethylene is increasing so rapidly that its mean concentration over the period cannot be computed, and calculate the values of K_p from the mean squared values of the ethylene concentrations, and the amount of condensate formed during consecutive intervals, we find that the value of the velocity constant tends to increase in a manner which has nothing whatever to do with the change in the ethylene concentration. When the process has proceeded for a certain time, which is about 3 hours at 590°, increasing at lower, and decreasing at higher temperatures, and diminishing generally at lower concentrations, either of two things may happen. At the higher temperatures the process suddenly slows down. At the lower temperatures the rate may slow down, or may be maintained so that the graph representing it is continuous. Graphs representing the process

² J.A.C.S., 1931, 53, 613.

at 590° and 570° are given in the paper referred to, and reproduced as Figs. 1 and 2 herewith, in which the crosses represent the results of experiments with plain reaction tubes at 590° and at 570° , respectively. It will be observed that at 590° the rates of formation of methane and of condensate are represented respectively by the graphs ab , $a'b'$, which are discontinued after about three hours, but at 570° the graphs ab , $a'b'$, are continued to c and c' . In both cases after bb' some of the points are below the continuation of ab , $a'b'$.

An interesting point to be noted is that the phenomenon of acceleration of the rate of the reaction in the case of pure ethane is associated

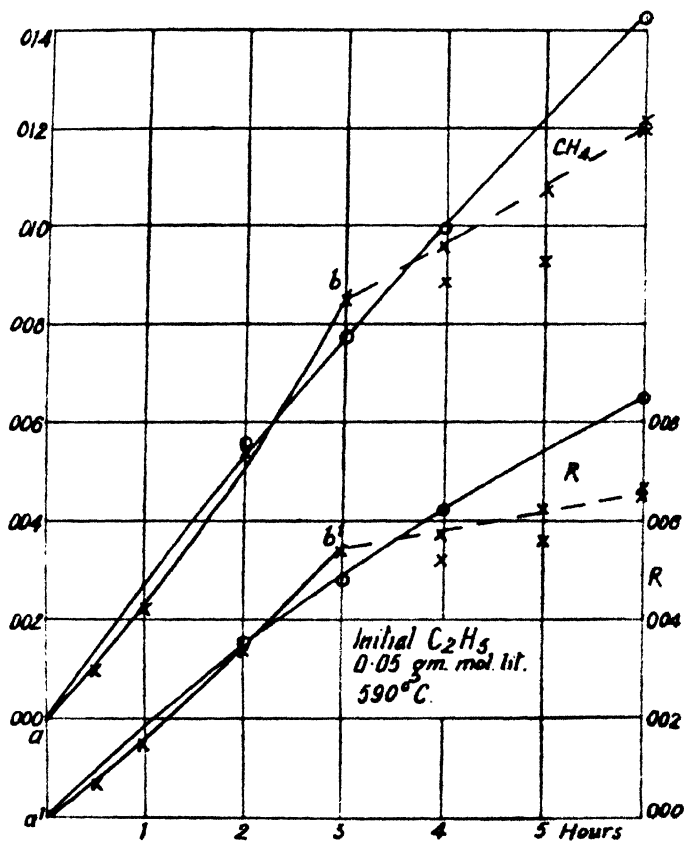


FIG. 1.

both with the formation both of methane and of condensate. Also, after the period within which all the points representing the rates of formation of methane and of condensate lie on the slightly upward-tending graph, if in any experiment a low result is obtained for methane, a correspondingly low result is obtained for condensate. The only connection between the two processes is that both products are derived from ethylene, and this fact must be regarded as the key to the solution of this part of the problem.

Now ethylene is formed from pure ethane by a process which has an activation energy of 75 K. Cal., the thermal requirements of the process

being only 31 K. Cal., leaving a balance of 44 K. Cal. to be dissipated by the ethylene and hydrogen. The share of energy carried by the ethylene may be passed on, and by a process somewhat similar to that occurring in the degenerate chain system of Semenov, increases the rate of formation both of primary centres which result in the formation of condensate and also of those which lead to the formation of methane. By this process both the rate of formation of condensate and the rate of formation of methane can be increased. The cause of the slowing down of the

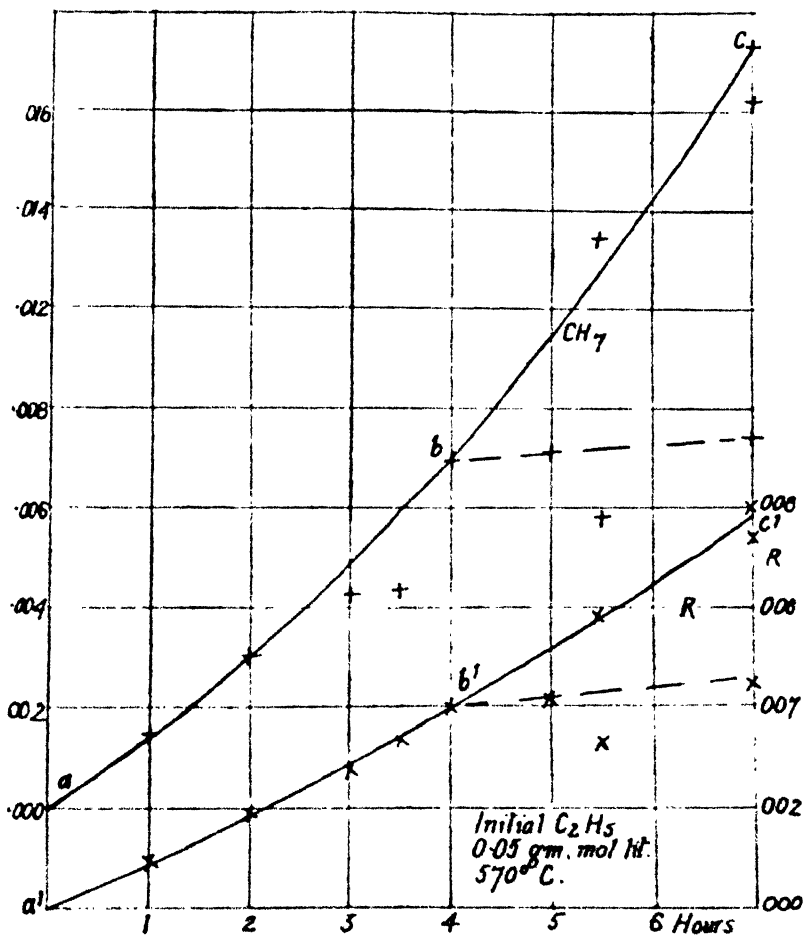


FIG. 2.

two processes has not been determined, but the rates after the breaks in the graphs seem to be close to the rates in the corresponding equilibrium mixtures.³

If we compute the rates for formation of condensate, K_p , for successive time intervals, omitting the first period, for which it is impossible to compute the concentrations of the ethylene accurately, and plot the values of K_p against the time from the zero time for the process, we find by extrapolation that the value of K_p for zero time, is not far from the mean

³ *Lec. cit.*, p. 333.

values for equilibrium mixtures at the corresponding ethane plus ethylene concentrations and temperature, but probably somewhat lower than

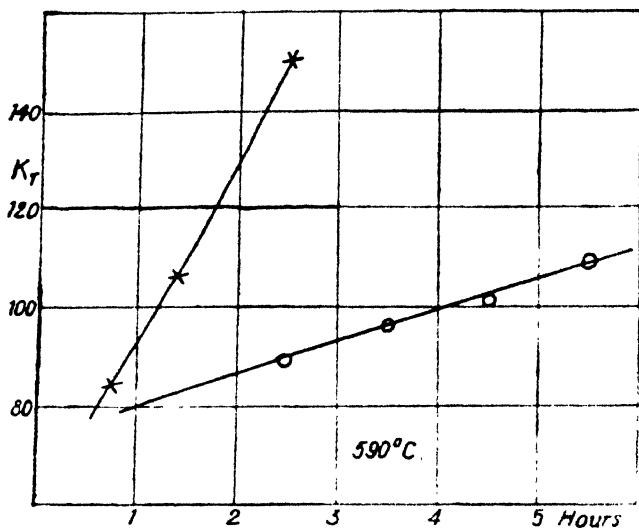


FIG. 3.

these values. This fact is demonstrated by the graphs in which represent the results of experiments with pure ethane, at 0.05 concentration, Fig. 3 at 590° (x empty tube, o tube packed with capillaries), and Fig. 4 at 570° (x plain tube, □ tube with two concentric linings). The values found

for equilibrium mixtures are 73 at 590°, and between 40 and 47 at 570°

Some experiments carried out with a view to finding out why, in experiments with pure ethane, in which the reaction tube had not been pre-treated with hydrogen, very erratic results were often obtained, had shown that the rate at which the primary decomposition of ethane took place varied with different tubes, and was most rapid in new silica tubes. In tubes which had the surface slightly increased by introducing two or three concentric lining tubes the effect was small, as indicated by Figs. 3 and 4, though it was noticed that the break in the graphs noted above was very marked. In Fig. 4 the points in squares were obtained using a tube containing two concentric tubes. However, when a tube was filled with capillary silica tubes⁴ it was noticed that the equilibrium in the system ethane—ethylene—hydrogen (590°) was very rapidly established, and the rates of formation of methane and

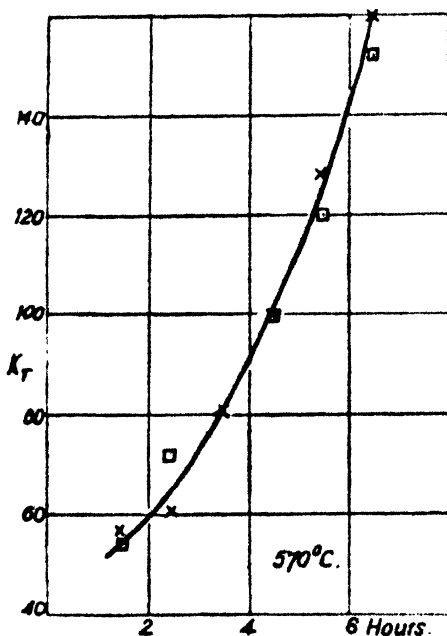


FIG. 4.

⁴ Loc. cit.¹, p. 337, Tables XV., XVI., Fig. 7.

condensate showed only very slight acceleration. The results are represented by the circles in Fig. 3. If, as in these experiments, the primary decomposition of the ethane took place on the surface, the energy of the process might be dissipated more readily than in the gas phase.

The particular behaviour of pure ethane may be accounted for by supposing that the number of primary centres is increased owing to the fact that some of the molecules of ethylene formed by the primary decomposition of ethane carry energy which they contribute to the process by which the centres arise. The process is superimposed on the process involved in the formation of condensate from an equilibrium mixture, which one would like to regard as a simple one, involving activation by collision of two molecules of ethylene, which subsequently react. However, when one comes to study the formation of condensate from pure

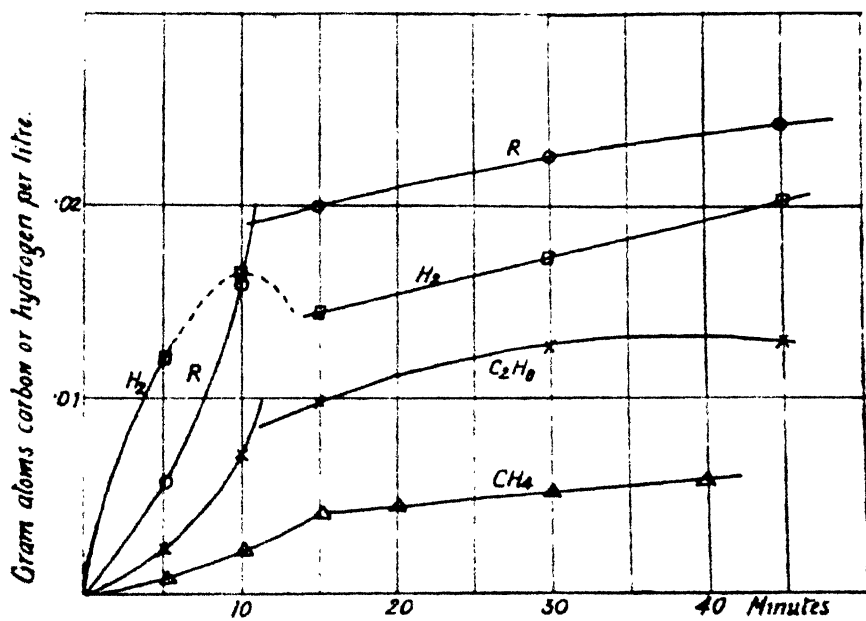
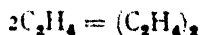


FIG. 5.

ethylene, one observes some disturbing facts. I must admit that this part of the investigation has been neglected.

Fig. 5 represents the changes taking place when pure ethylene at initial concentration 0.05 gram atoms of carbon per litre is heated at 500°, the details being given in Table II. The process is obviously complex, for while the primary condensation process may be represented by



the rapid changes which follow result in the liberation of hydrogen, which takes part in secondary minor processes involving the formation of ethane and of methane.

Now the most obvious fact is that the rate of formation of condensate increases rapidly, while the concentration of the ethylene diminishes. One might expect that the initial rate, determined graphically, would give a value for the rate constant (K_p) of about the same value as that

TABLE II.—EXPERIMENTS WITH PURE ETHYLENE.

Temperature 500°. Initial concentration 0.05 gram atoms carbon per litre.

Time (mins.).	C ₂ H ₄ Found.	C ₂ H ₆ .	CH ₄ .	H ₂ .	Condensate.
5	0.04107	0.00214	0.00050	0.00122	0.00550
10	0.02454	0.00718	0.00220	0.00164	0.01590
15	0.01598	0.00978	0.00420	0.00140	0.02004
30	0.00048	0.01204	0.00531	0.00176	0.02257
45	0.00652	0.01298	0.00630	0.00202	0.02420

obtained by the same method for equilibrium mixtures of the same initial concentration, and at the same temperature, *viz.* 73. However, the apparent value for the initial velocity is only about 20, and the real value may be considerably less. The mean calculated value for the period 0 to 5 minutes is about 31, and for the period 5 to 10 minutes about 107. The break occurs within the next five-minute interval, and during the two following 15-minute intervals the values are 60 and 98 respectively.

A very few experiments have been carried out with pure ethylene but they seem to indicate that the results are influenced to a considerable extent by the condition of the surface of the tube, and that it is difficult to obtain reproducible results. As soon as the apparatus, which is in use for other work, is available, the investigation will be followed up.

There are two possible alternative explanations of the behaviour of ethylene. In the first place we can assume that the process is initially a bimolecular one, and that the 4-carbon product resulting undergoes further association, and there seems to be direct chemical evidence that this process actually operates at low temperatures. The alternative is that a series of 2-, 3-, 4-carbon products are formed.

If we adopt the former alternative we must assume that the energy set free in the process,

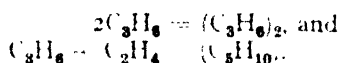


is taken up by ethylene molecules, some of which contribute their share of the energy to the formation of new primary centres. The fact that in equilibrium mixtures the rate of formation of condensate is only 1/10,000 of the rate calculated on the assumption that the energy of activation is 35 K. Cal., making the usual assumptions as to molecular diameters, etc., suggests that the formation of condensate requires the dispersion of the energy of the bimolecular process by a third body. In the case of the equilibrium mixtures, the energy is taken up mainly by the ethane, and simply dispersed. In the case of pure ethylene, during the early stages, when only ethylene is present, the energy can only be taken up by ethylene molecules, and since these can react a chain process results. It seems likely that either of the mechanisms which operates in the case of pure ethane, or that which operates in the case of pure ethylene, disappears to a great extent in the case of equilibrium mixtures, which do not approach very closely to one end or the other of the series; for none of the phenomena associated with chain mechanisms are present. The increase of the rate of formation of condensate in equilibrium mixtures with increase in the total initial hydrocarbon content, may be due to increase in the rate of formation of primary centres, or to third-body action. Silicon tetrafluoride may exert a similar influence.

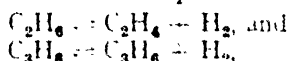
The primary step in the formation of condensate from ethylene appears to be a bimolecular process, the rate of which is influenced by several factors the nature of which has been discussed. There is no evidence as to how compounds of high molecular weight are formed for the primary product.

The System Propane—Propylene—Hydrogen.

Sufficient work has been carried out in the neighbourhood of 550° to indicate the general course of the processes taking place. However, the problem is complicated by the fact that propylene decomposes in the presence of hydrogen yielding ethylene and methane, the mechanism being probably that suggested by Dr. Pearce and myself to account for the formation of methane from ethylene. At the same time two condensation processes take place, the primary steps in which may be represented by—



The particular difficulty in the work, apart from the problem of analysis, which is certainly complex and tiresome, is due to the fact that we have always in the background the two equilibrium systems,



which, under the temperature conditions which are convenient for the investigation, appear to be partly heterogeneous, so that it is difficult to obtain reproducible results.

The work is important, particularly as it may throw light on the general questions involved in the cracking and condensation of hydrocarbons generally.

Acetylene.

There is a considerable literature relating to this subject which is collected in a recent paper by Taylor and van Hook.⁵ These authors confirm the conclusion previously

TABLE III.

THE ACTION OF HEAT ON ACETYLENE AT 450°

Time (hours)	C.c. C_2H_2 Taken.	C.c. C_2H_2 Found.	C.c. C_2H_2 Reacted.	H_2
0.5	0.41	7.33	2.08	0.124
0.75	0.35	6.08	3.27	0.170
1	0.42	4.97	4.45	0.275
1.5	0.42	4.46	4.90	0.385
2	0.43	3.88	5.55	0.447
0.5	18.01	10.25	8.66	—
0.75	18.01	8.32	10.59	—
1.25	18.02	1.58	17.34	—

They explain the latter on the assumption that some of the acetylene is hydrogenated, but make no attempt to ascertain whether this really happens or not. Their conclusions are based almost exclusively

⁵ *J. Physic. Chem.*, **39**, 810.

on the results of pressure measurements at constant volume between 400° and 500°.

Dr. Hockin and I carried out a few exploratory experiments at 450°, using a silica tube of 35 c.c. capacity. In Table III. are the results at two concentrations.

The graph representing the first series showed a definite break in the middle, the first part being linear. The graph representing the second series is linear. That the slopes of the two graphs are nearly proportional to the squares of the initial concentrations may have no direct significance. The addition of hydrogen increases or decreases the velocity of the reaction, according to its concentration. When much hydrogen is added, some methane is formed, but apparently very little ethylene. The state of the silica surface has a considerable influence on the nature of the reaction.

These figures are quoted because I wish to make it clear that the mechanism of the polymerisation of acetylene is only likely to be explained when full experimental data are forthcoming. Speculations based upon measurements of changes of pressure are likely to confuse the real issues.

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ON TWO NEW POLYMERS OF ACETALDEHYDE.

By MORRIS W. TRAVERS.

Received 7th August, 1935.

1.

Acetaldehyde, like many other organic liquids, dissolves very considerable quantities of air. For the purpose of studying the thermal decomposition of the liquid it was necessary to obtain it oxygen-free.

With this object in view, after drying over potassium sulphate, and fractionating using a long column, the temperature of which was controlled, the liquid was syphoned into the large bulb, A, of the apparatus shown in Fig. 1. The bulb was then cooled with solid CO₂ and alcohol, and the leading-in tube was sealed at *a*. The three bulbs had capacities approximately 500, 250, and 150 c.c. respectively, and they were partly filled with pieces of glass tubing. The apparatus was connected with a bulb which formed part of the apparatus for filling the reaction tubes for the thermal study, and through this apparatus, and a U-tube immersed in liquid oxygen, with a Töpler pump.

While the bulb A was cooled to near - 80° the whole apparatus was exhausted, and as acetaldehyde has a perceptible vapour pressure at this temperature, a little vapour condensed in the guard tube. The bulb A was then allowed to warm up to about - 60, and the bulb B was cooled in liquid oxygen, the Töpler pump being operated the whole time. While the liquid was distilling from A to B a considerable quantity of gas, mainly oxygen, was collected. When the bulb B was about two-thirds filled with liquid the connecting tube was sealed at *b*. During this operation both the bulbs A and B were cooled in liquid oxygen.

The bulb B was then warmed to about -60 , and the bulb C was cooled in liquid oxygen. During the second distillation a little gas was collected, but when the bulb C was two-thirds filled with liquid the evolution of gas had practically ceased. The connecting tube was then sealed at *c*.

In the early operations part of the liquid was then distilled from C into D by the same process, but in later operations, for reasons to be mentioned directly, the final distillation was carried out by evaporating the liquid from air temperature into the receiving bulb cooled in ice. However, before sealing the connecting tube both bulbs were cooled with liquid air, to avoid decomposing aldehyde vapour.

Now we noticed that when air-free acetaldehyde was condensed at liquid air temperature, instead of obtaining a mobile liquid, the receiving bulb was found to contain a more or less viscous liquid or even a jelly. The viscosity of the product seemed to depend upon the extent to which

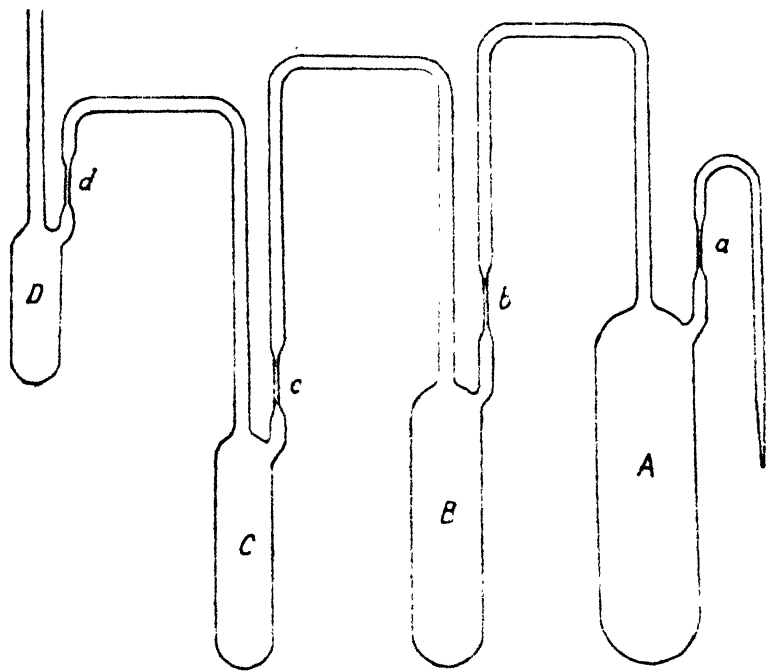


FIG. 1.

the air had been eliminated before the particular fraction was distilled, the content of the bulb B being less viscous than the contents of the bulb C, and the contents of C less viscous than the contents of D. If the contents of a bulb was viscous before redistilling, on distillation *in vacuo*, even from air temperature, it became more viscous, or even jelly like. However, the bulb D was connected with an apparatus by which its vapour pressure could be measured, and it was found that the vapour pressure of a jelly or viscous liquid was not measurably less than that of the mobile liquid.

If a bulb containing the viscous liquid was connected with an exhausted apparatus cooled to a low temperature, without admitting air in the process, the contents frothed, forming a vesicular mass, which, in time, settled down to an almost glassy material, apparently quite stable at the air temperature. At 100° , in a sealed tube, acetaldehyde was slowly regenerated.

I have had no opportunity of carrying out experiments with this substance, much less of investigating the mechanism of its formation. I have no intention of following up the study of it, and I should be glad to hear that someone else is doing so. It is clear from the method by which it is formed that air inhibits the process. Surface favours the formation of the jelly, and the state of the surface seems to be of some importance, for it was sometimes noticed that the jelly formed in particular regions of the surface of a bulb in which air-free acetaldehyde was condensed. It is most readily obtained by distilling air-free acetaldehyde into a bulb cooled in liquid air, the liquid evaporating from the air temperature.

The product seems to belong to the class called by Chalmers and others *macrocolloids*, which are formed by the addition of comparatively small units, successively, to form long molecular chains. To this class belong substances like rubber, and possibly cellulose. The energy of activation must be very small, if, indeed, the energy of activation comes into the picture at all. The inhibition of chain formation by gases must also be a physical process. On the other hand there must be a not inconsiderable free energy change accompanying the process of polymerisation.

II.

(WITH MR. R. G. SOLLERS, B.Sc.)

The observations recorded above suggested an experiment on the polymerisation of acetaldehyde in presence of acid at low temperatures.

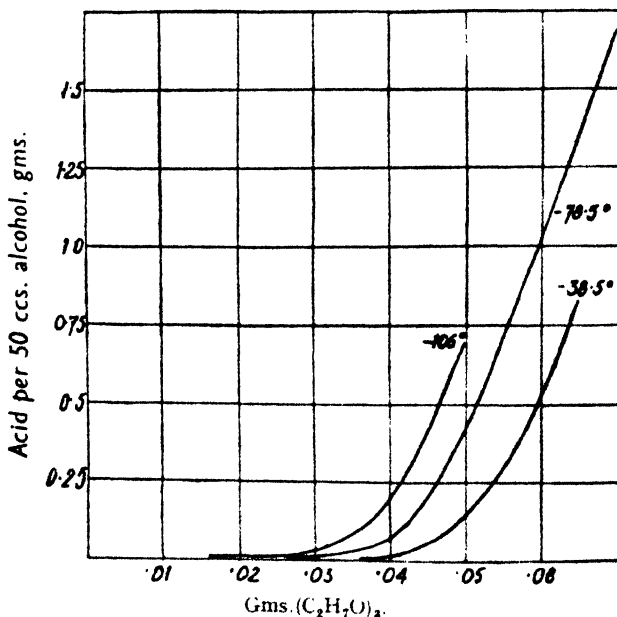


FIG. 2.

for though it is very well known that two compounds, metaldehyde and paraldehyde, are formed, literature tells us very little as to details. A small quantity of pure acetaldehyde was cooled to -80 , and to the liquid was added a drop of an alcoholic solution of sulphuric acid. It was noticed that the contents of the tube containing the acetaldehyde solidified completely, but that, on warm-

ing to air temperature, very little metaldehyde could be separated by filtration. On distilling the liquid it was found to boil at $73^\circ-75^\circ$, with some decomposition into aldehyde, and condensation to higher-boiling

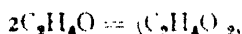
products. Its molecular weight by the cryoscopic method was close to that corresponding to $(C_2H_4O)_3$; and the vapour density determination at 100° showed that the compound had, initially, the formula given above, but that it dissociated rapidly.

The following experiments were carried out with a view to studying the formation of the substance. A quantity of acetaldehyde, 4.08 c.c. was placed in a test tube, and cooled to a definite temperature, which was either -38.5° , -78.5° or -105° , the latter being well above the melting-point of aldehyde, which is -125° . A quantity of an alcoholic solution of sulphuric acid 0.08*N*, freshly made, was then run into the aldehyde from a pipette, the liquid being shaken. After remaining at rest at the temperature of the experiment for a fixed time, the liquid was warmed to the air temperature, and the metaldehyde was filtered off on a Gooch crucible, and, after washing with a few drops of alcohol, it was weighed. The data for three sets of experiments are represented by the graphs in Fig. 2, the quantities of metaldehyde formed being plotted against the strength of the acid added.

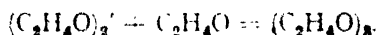
The whole process seems to be a very rapid one at any of the temperatures at which the results are recorded, for the time between adding the acid, and warming up and filtering the liquid made no perceptible difference to the quantity of metaldehyde formed. For equal acid strengths, between -105° and -38.5° the quantity of metaldehyde increases as the temperature rises, but, at higher temperatures still, the quantity decreases, and the liquid contains some paraldehyde.

The data refer to a single sample of acetaldehyde; but using a different sample, also supposed to be pure, for a series of experiments at -78.5° , the graph representing the results had a slightly different slope. This suggests inhibition of one process or the other by a trace of some impurity.

The experiments throw no direct light on the problem of formation of either of the two bodies metaldehyde or paraldehyde, both of which are said to have the formula, $(C_2H_4O)_3$. It seems likely, that the first step is the formation of the dialdehyde,



and that a second step may be represented by,



the activation energy being derived from the first process. A somewhat inconclusive experiment indicated that a mixture of the dialdehyde with acetaldehyde did not yield metaldehyde. An alternative suggestion is that the primary formation of the dialdehyde is followed by rapid internal rearrangement, and the reasons for the stopping of the polymerisation process at the second and third stages respectively are really steric. Possibly the two alternatives are really identical.

Bristol University.

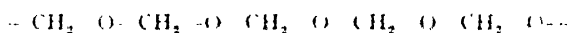
GENERAL DISCUSSION.

Professor A. Staudinger (*Freiburg i Br.*) said: The very interesting polymerisation product of acetaldehyde which Professor Travers has just described is presumably a eucolloidal polyacetaldehyde. This can be concluded from the high viscosity and particularly from the elastic properties of this product, for such physical properties only arise in the case of very high molecular weight products of eucolloidal nature.

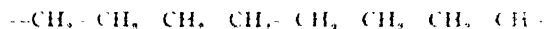
An analogous polymerisation product can be prepared by polymerisation of pure formaldehyde under conditions which are very similar to those of the polymerisation of acetaldehyde. In the polymerisation of formaldehyde in the presence of acid or alkali only hemicolloidal products of a polymerisation degree of approximately 100 are obtained and according to the reaction conditions α -, β -, or γ -polyoxymethylenes.¹ These hemicolloidal polyoxymethylenes are powder-like substances. On the other hand in the polymerisation of pure formaldehyde one obtains a hard glassy mass which can also be got in the form of transparent films of remarkable strength.² When heated, this product becomes elastic and therefore it must be assumed that this product has a much higher degree of polymerisation than the hemicolloidal powder-like products, since only high molecular weight products of a degree of polymerisation of the order of 1000 and above possess elastic properties.³ The molecular weight of this eu colloidal polyoxymethylene cannot, however, be determined, since the substance is completely insoluble. On account of this the new polyacetaldehyde which is soluble in organic solvents becomes very interesting. The differences in solubility between polyoxymethylene (polyformaldehyde) and polyacetaldehyde depend upon the fact that the former products have unbranched straight chains, whereas the polyacetaldehyde has methyl groups as side chains. The more irregular shape of the latter molecule is the cause of its greater solubility. Similar experiences were found in the case of the paraffins. Normal paraffins are scarcely soluble. The introduction of the methyl groups causes a considerable increase in their solubility so that the high molecular weight methyl substituted paraffins (compare also rubber) are soluble in organic solvents:⁴

I Insoluble high molecular weight compounds:

Polyoxymethylene:

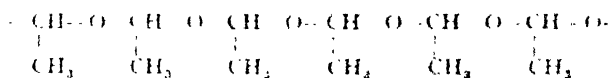


Paraffins:

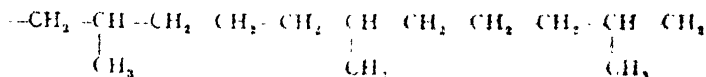


II. Soluble high molecular weight compounds:

Polyacetaldehyde:



Hydrorubber:



¹ Compare H. Staudinger and collaborators, *Ann.* 1929, **474**, 145-275; further H. Staudinger and M. Luthy, *Helv. chim. acta*, 1924, **8**, 41.

² Compare H. Staudinger and W. Kern, *Die hochmolekularen organischen Verbindungen, Kautschuk und Cellulose*, Berlin, 1932, p. 255.

³ On the relation between elasticity and molecule size compare my book, *loc. cit.*, p. 121.

⁴ Compare H. Staudinger and L. O. Leupold, *Helv. chim. acta*, 1932, **15**, 324.

POLYMERISATION OF UNSATURATED HYDROCARBONS.*

BY H. I. WATERMAN AND J. J. LEENDERTSE.

Received 19th July, 1935.

Introduction.

The authors have sought to investigate how far the polymerisation phenomena of olefines under moderate conditions accord with true polymerisation. In certain special cases hydrocarbon mixtures poor in ring-compounds, in other cases products rich in ring-compounds may be required by industry. We had eventually, therefore, to study the conditions which are necessary to prevent molecular rearrangements and transformations which lead to the formation of saturated paraffinic hydrocarbon polymers on the one hand and of systems poorer in hydrogen on the other. The components rich in ring-compounds which are so often found in the reaction products, especially in the fractions of higher molecular weight, would be formed by the said rearrangements and transformations.

Method of Investigation.

The usual methods were used in this investigation with the exception of a new method for the separation of the fractions of different molecular weight without any decomposition. For this purpose we applied the method of distilling in cathodic-ray vacuum tubes with internal means for the condensation of the distillate. The sum of the fractions thus obtained could be considered as representing the total original reaction product, no destruction having occurred during distillation. The fractions were investigated by the so-called "ring analysis," determining, *inter alia*, the specific refraction

$$\left(\frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{d} \right)$$

* Compare H. I. Waterman, G. F. de Ridder and J. P. Kuipers, "Contribution to the knowledge of polymerisation," Part I, *J. Inst. Petroleum Technologists*, 1929, **12**, 506; H. I. W. and J. C. Jansen H., *Ibid.*, 1926, **12**, 510; H. I. W. and A. J. Tulleners, "Decomposition of ethylene by heating under pressure," *Ibid.*, 1931, **17**, 500; H. I. W. and A. J. L., "La polymérisation catalytique de l'éthylène," *XII^{me} Congrès de chimie industrielle, Prague, Septembre, 1932, Chimie et Industrie*, 1933, **29**, 496-505; H. I. W., J. J. Leendertse and A. J. T., "On the behaviour of the pentenes with branched chains towards hydrochloric acid and aluminum chloride at low temperature," "Method for the preparation of isopropylethene," *Rec. trav. chim.*, 1933, **52**, 515; H. I. W., J. Over and A. J. T., "Polymerisation of isobutene," *Ibid.*, 1934, **53**, 690; H. I. W., J. J. L. and A. J. T., "On the behaviour of the pentenes with branched chains and the normal pentenes towards hydrochloric acid and aluminum chloride at low temperature," *Rec. trav. chim.*, 1934, **53**, 715; H. I. W., J. J. L. and A. J. de Kok, "Polymerisation of isobutene with aluminum oxide on silica gel as a catalyst and the addition of HCl-gas to the reaction products without a catalyst," *Ibid.*, 1934, **53**, 1151; H. I. W., J. J. L. and W. M. Klazinga, "Polymerisation of pentenes," *Ibid.*, 1935, **54**, 79; H. I. W. and J. J. L., "The physical constants of the polymerisation products of unsaturated hydrocarbons," *Ibid.*, 1935, **54**, 130; H. I. W., J. J. L. and A. C. ter Poorten, "Polymerisation of cyclohexene," *Ibid.*, 1935, **54**, 245.

and mean molecular weight and other physical constants of the saturated fractions. This method, which will be described more thoroughly in another paper¹ comprises also a careful non-destructive hydrogenation of the fractions obtained in polymerisation.

Polymerisation of Ethylene.

Ethylene was polymerised under high pressure at 125°-150° C., with AlCl_3 as catalyst and with pentane as a liquid diluent. The results of the experiments and the analysis of the fractions are represented in Fig. 1. The points in the figure relate to the completely hydrogenated fractions of the polymerisation product.

The fractions obtained from the free oil (A) were plotted on curve I., and, in addition, three fractions derived from the oil (B) liberated from the sludge after decomposition with ice water, were combined in curve II., as is indicated in the figure.² It was proved that the low boiling light fractions of the A oil without any further treatment were saturated and paraffinic,³ which must be ascribed to an interchange of hydrogen. The higher fractions of the A oil are somewhat cyclic and the number of rings per molecule increases with increase of molecular weight. The fractions with a molecular weight of 250 to 350 contain on an average about one ring per molecule, whereas a fraction with the molecular weight 530 contains 2 rings per molecule. The B oil fractions are much richer in rings than the A fractions. The cyclic character is more dominating here, e.g., a product with molecular weight 365 contains more than 3 rings per molecule. An increase in molecular weight of the B fractions is connected with a stronger increase in the number of rings per molecule. A. W. Nash and Stanley² obtained analogous results. The advantage of the present investigation is that one gets a better survey of the nature of all the fractions, i.e., the cyclic character is determined by a number (compare Fig. 1).

The question might arise how far the cyclic character really is caused by the presence of rings. Could not the deviation of the specific refraction be explained by the presence of special branched hydrocarbons? In order to answer this question an ultimate analysis was carried out with a series of analogous fractions, from different polymerisation products of other olefines. It was thus proved that the inference derived from the specific refractive molecular weight diagram that the substances are cyclic is approximately correct, since this is in accordance with the ultimate analysis.

The observed presence of cyclic compounds may be explained by the considerations mentioned below:

(1) Aluminium chloride is a somewhat active catalyst and this factor, combined with a relatively high temperature 125-150° C., will increase the tendency of ring formation.

(2) Since we are using an olefine of low molecular weight, i.e., ethylene, the number of polymerisations and eventually connected rearrangements and transformations must be high if products of high molecular

¹ J. C. Vlughter, H. I. Waterman and H. A. van Westen, "Improved methods of examining mineral oils, especially the high boiling components," *J. Inst. Petr. Tech.*, July and August, 1935.

² The designations A and B were used by A. W. Nash and A. M. Stanley, *J. Inst. Petroleum Technologists*, 1930, 16, 830.

³ The light boiling fractions boiling below about 100° C.

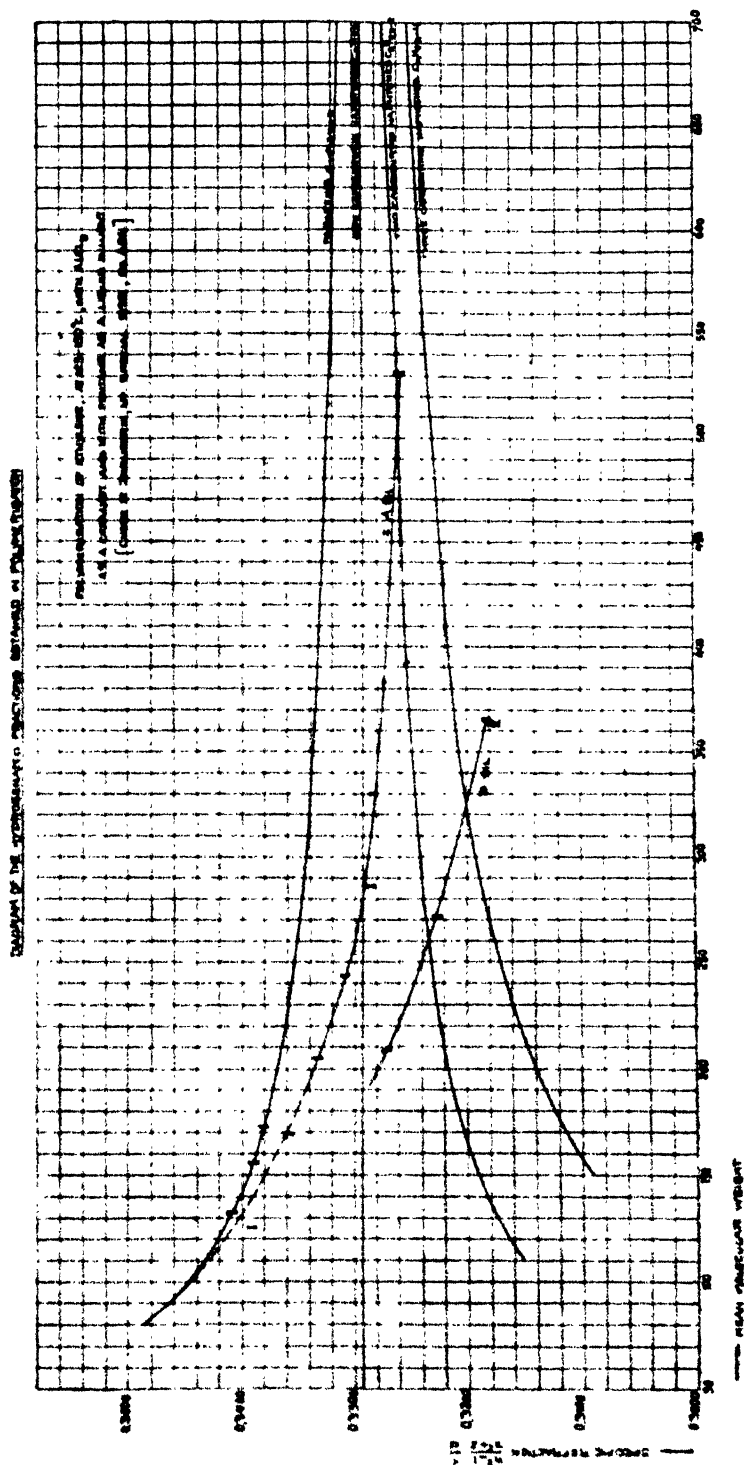


FIG. 1.

weight are formed. Therefore the chances of ring formation are better in this case than with olefines of higher molecular weight.

Polymerisation of Isobutene.

It was proved that the polymerisation of isobutene with aluminium oxide on silica gel as catalyst at about 40° C. can be carried out practically without any formation of rings. The fractions were truly olefinic in nature and therefore after hydrogenation paraffinic in structure (compare Fig. 2). The curve which connects the different hydrogenated fractions lies close to the paraffin curve (C_nH_{2n+2}).

Aluminium chloride seems to be an extraordinarily active catalyst when we consider that even at - 80° C. the reaction is nearly explosive. Several polymerisations were carried out at low temperature working at - 35° to - 40° C. and at + 7° to + 16° C. with pentane as a liquid diluent. It seems that the higher polymerised fractions in this case are somewhat cyclic. The curve which connects the hydrogenated fractions at higher molecular weight lies below the curve of the paraffins (C_nH_{2n+2}).

Attention must be given to the fact that the fractions of high molecular weight are very sticky and viscous.

Polymerisation of Pentenes.

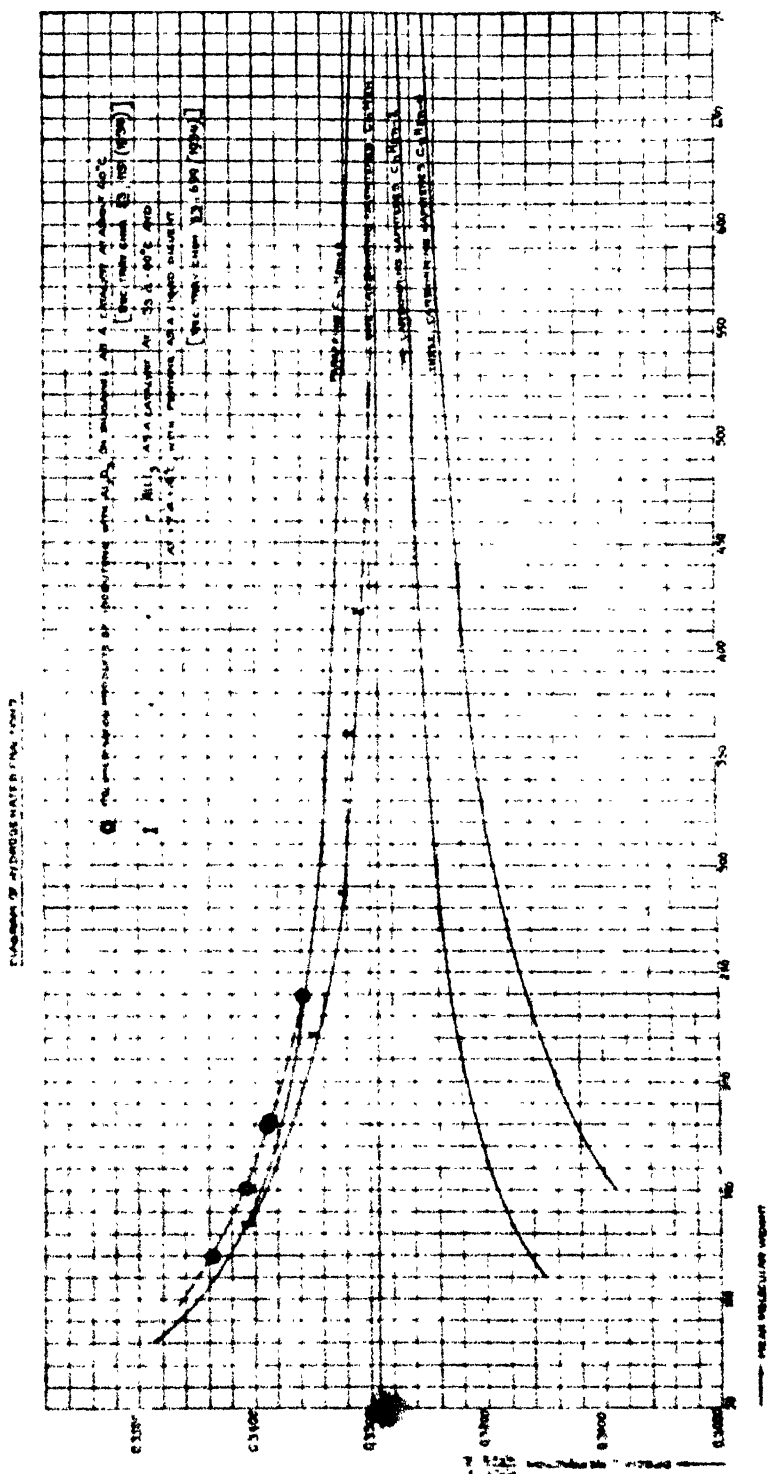
The pentene experiments proved that aluminium chloride even at relatively low temperatures 0° to - 80° C. can cause a formation of rings. Experiments with normal 2-pentene at 0° C. yielded fractions which at a molecular weight of about 350 contained 1 ring per molecule. The branched pentenes at - 80° C. also yielded partly cyclic fractions.

An increase of the temperature to about 400° C. with or without alumina as a catalyst, causes an increase of the cyclic character of the polymerisation products of *n*-2-pentene, but with the branched pentenes, on the other hand, this influence if present, was smaller.

Polymerisation of Hexadecene * (experiments carried out by J. G. Frielink).

A polymerisation was carried out with boron fluoride as catalyst; the reaction temperature was 10 to 15° C., the duration of this experiment several hours. We worked with a stream of boron fluoride. The yield of polymers was 70 per cent. of the raw material. A second experiment was done with aluminium chloride, the temperature was 17-23° C., the duration of this experiment was 3½ hours, the proportion of catalyst used was 6 per cent., and it was added gradually. The yield was about 95 per cent. The results of the two experiments are represented in Fig. 3. In the first experiment the total reaction product was divided into three fractions of mean molecular weight 235, 460 and 728, determined after careful hydrogenation. In the $AlCl_3$ polymerisation there was obtained only a product of high molecular weight 1482 after hydrogenation). In both experiments the hexadecene polymers proved to be free from cyclic compounds. It may be remarked that the viscosity-temperature curve for the hexadecene polymers, before and after hydrogenation, is more flat than the corresponding curves of isobutene and several pentene polymers.

* The product obtained by decomposition of spermaceti, was probably a mixture of normal hexadecenes, not contaminated with branched olefines.



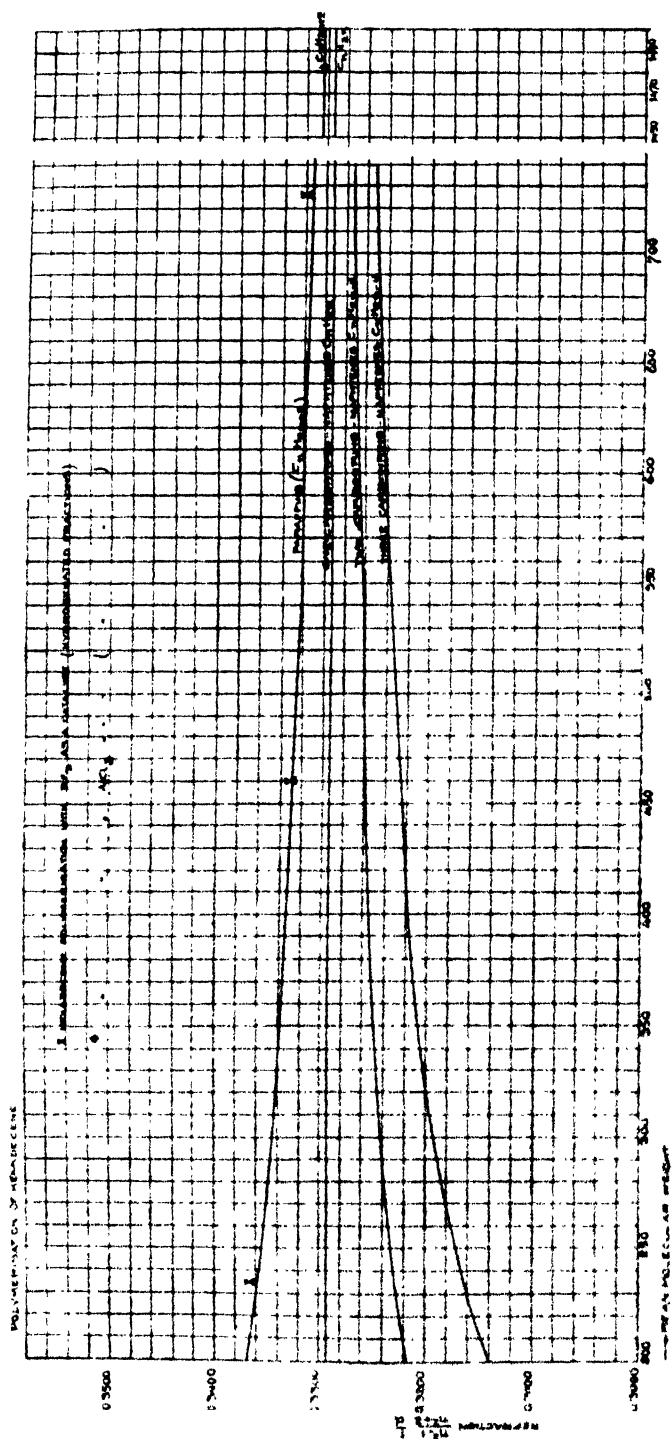


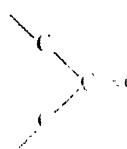
FIG. 3.

Polymerisation of Cyclohexene.

In the polymerisation of cyclohexene at 70°C ., high molecular products were obtained, which after complete hydrogenation had a specific refraction in agreement with the calculated figures for cyclohexyl compounds of the same molecular weight. Thus, for example, at a molecular weight 400 the product contained about 5 rings per molecule. So in this case the observed phenomena may be explained by true polymerisation.

Reaction Velocity of Polymerisation of the Olefines at -80°C .

The velocity of polymerisation depends on the molecular structure of the raw materials at -80°C . especially, there are pronounced differences. It seems that if the double bond between two carbon-atoms

is connected with the structure , there is a marked increase

in the polymerisation velocity at -80°C ., e.g., isobutene reacts at -80°C much more strongly than the two normal butenes with aluminium chloride as a catalyst. Analogous differences are found with the homologues, although the reactivity generally decreases with increasing molecular weight.

Summary.

Several fractions obtained by polymerisation of olefines, were completely hydrogenated and investigated by the so-called ring analysis method.

The number of rings for hydrogenated polymerisation fractions read in the specific refraction molecular weight diagram practically is in accordance with the results of ultimate analysis.

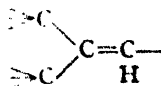
It was found that the formation of rings is connected with the polymerisation, especially for low molecular olefines with aluminium chloride as a catalyst, even at low temperature, e.g., -80°C .

True polymerisation not leading to ring formation was observed in the polymerisation of hexadecene at room temperature and with aluminium chloride and boron fluoride as catalyst.

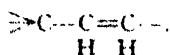
Ring formation was not observed in the polymerisation of isobutene at 40°C with aluminium oxide on silica gel as catalyst.

By the polymerisation of cyclohexene products are obtained which seem to be completely cyclic, which is explained by true polymerisation.

At -80°C with aluminium chloride as a catalyst the polymerisation velocity of olefines of equal molecular weight depends *inter alia* on the structure, the group



causes a higher activity than the group



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Technical University.*

GENERAL DISCUSSION.

Dr. E. Bergmann (*Rehoboth*) said: It is rather striking that the only ethylene homologue, the polymerisation of which does not lead to cyclic products is isobutene, containing one quaternary C-atom. All the others which have been investigated are of the type $\text{RHC}=\text{CHR}$. Since, on the other hand, it is known that AlCl_3 , used by the authors as a catalyst, readily dehydrogenates organic compounds, the suggestion may be made that the formation of cyclic products is due to previous dehydrogenation to form either acetylenes or dienes, the former being polymerisable to benzenoid compounds, the latter to cyclic substances of the menthadiene type.

Professor H. I. Waterman (*Delft*), in reply, said: In the examples given for isobutene, the formation of rings was not important and can be explained by the consideration, that the temperature was very low in the experiments mentioned. The ethylene polymerisation experiments were done at a higher temperature (*e.g.*, 125° to 150° C.). The conditions (*e.g.*, temperature) have a striking effect on the molecular structure of the polymerisation products.

THE MERCURY PHOTOSENSITISED POLYMERISATION OF ACETYLENE

BY H. W. MELVILLE.

Received 10th July, 1935.

Investigations on polymerisation processes have almost wholly been designed with a view to controlling the nature of the products of the reaction—a circumstance only to be expected from the importance polymeric substances have assumed in technical practice. On the theoretical side of the question little has been accomplished, for the good reason that the mechanism of the reactions undergone by comparatively simple molecules is still the subject of much controversy. At first sight it would appear to be impossible to attempt to analyse the mechanism of polymerisation of even the simplest molecules by means of the well-established methods of chemical kinetics. Kinetic methods are, however, not quite so restricted in their scope. Whilst their primary aim in dealing with complex reactions is to unravel the sequence of collision types which comprise such processes, much reliable information may be gathered from an examination of almost any complex reaction over a sufficiently wide range of operating conditions. In polymerisations there is fortunately a simplification which permits the analysis to be made more detailed than might otherwise have been the case. The properties of the growing polymer are certainly a continuous function of its size, so that, although a considerable number of different molecular species has to be considered, these molecules obey similar kinetic laws in their reactions with each other or with unpolymerised reactants. In this paper an attempt will be made to apply kinetic analysis to the polymerisation of acetylene in order to gain some idea of the type of collisions responsible for the initiation, propagation and cessation of the growth of the polymers.

A first step in elucidating the nature of polymerisation has been

taken by studying the molecular statistics of dimerisations. Vaughan¹ has shown that the dimerisation of ethylene, butadiene and isoprene are slow reactions in the sense that the observed bimolecular velocity constants are much smaller than those calculated from the measured energy of activation and supposing two square terms to supply the energy. This would imply that such molecules must be oriented in a particularly favourable position before association may occur. Since the dimerisation of simple molecules exhibit large steric factors, it is evident that such factors will play a part in the building up complex polymers.

The polymerisation of acetylene has been studied by a number of investigators. Berthelot and Gaudechon,² Bates and Taylor,³ and Reinke⁴ showed that when exposed to the full radiation of a "hot" mercury lamp, that is, under conditions where the mercury sensitised reaction is probably absent, acetylene is converted to an inert solid at room temperatures. In a similar way α -particles⁵ lead to polymerisation, the surprising result being that the number of molecules polymerised per ion pair is 20. Lind and Livingston⁶ made the interesting observation that the quantum yield of the direct photochemical reaction is about nine, using a mercury lamp as source and paying particular attention to the exclusion of mercury vapour. Likewise in the electric discharge,⁷ the number of acetylene molecules polymerised per ion pair is comparable with that obtained by the action of α -particles. Not much is known about the product of the reaction except that its empirical formula is $(C_2H_2)_n$. It is noteworthy that the polymerisation is attended with little complication in respect of secondary decomposition, for no hydrogen or methane can be detected in the products (see below). The product must be of considerable molecular weight, for it is only sublimed in a vacuum of 10^{-5} mm. with partial decomposition at temperatures in the neighbourhood of 300°. Kemula and Mzrzek⁸ have, however, detected, spectroscopically, traces of benzene during the photochemical polymerisation at room temperatures. On prolonged illumination at 175-250° acetylene yields isolatable quantities of benzene besides a considerable amount of polymer.⁹ Acetylene also polymerises¹⁰ if heated above 400° at a pressure of several hundred millimetres, but the kinetic interpretation of the data is rather difficult.

Ethylene too may be polymerised by exposing to the full radiation of the mercury lamp² or by collisions with excited mercury atoms.¹¹ The reaction is more complicated than that of acetylene. It has been shown qualitatively¹² that both methods of stimulation yield acetylene as primary products and therefore it is not improbable that the real polymerisation reaction is that of acetylene, the polymer of which is

¹ Vaughan, *J. Amer. Chem. Soc.*, 1933, **55**, 4109.

² Berthelot and Gaudechon, *Comptes rend.*, 1910, **150**, 1160.

³ Bates and Taylor, *J. Amer. Chem. Soc.*, 1928, **49**, 1144.

⁴ Reinke, *Z. anorg. Chem.*, 1928, **41**, 1144.

⁵ Bardwell and Lind, *J. Amer. Chem. Soc.*, 1926, **48**, 1559.

⁶ Lind and Livingston, *ibid.*, 1932, **54**, 94.

⁷ Lind, *Trans. Amer. Electrochem. Soc.*, 1931, **59**, 141.

⁸ Kemula and Mzrzek, *Z. physik. Chem.*, 1934, **23B**, 350.

⁹ Livingston and Schufflett, *J. physik. Chem.*, 1934, **38**, 377.

¹⁰ Brunner, *Helv. Chem. Acta*, 1930, **13**, 1130. Pease, *J. Amer. Chem. Soc.*, 1929, **51**, 3470.

¹¹ Olson and Meyers, *J. Amer. Chem. Soc.*, 1926, **48**, 389; 1927, **49**, 3131.

¹² Mooney and Ludlam, *Trans. Faraday Soc.*, 1929, **25**, 442. Taylor, *ibid.*, 1920, **21**, 500.

simultaneously reduced by the hydrogen liberated in the primary dissociation. In the thermal reaction ethylene, unlike acetylene, appears only to form dimers after which the process stops.

In the following pages the above-mentioned experiments have been extended by examining further the polymerisation of acetylene and ethylene under the influence of excited mercury atoms. An attempt is then made by combining older data with the new, to gain some general idea of the type of collisions responsible for the formation of the polymer.

Experimental.

Several types of reaction vessel were used. The final arrangement adopted consisted of a silica bulb attached to a small mercury diffusion pump¹³ to circulate the gas through traps, the inner surface of which was coated with mercury droplets. This precaution was taken in order to keep the mercury vapour pressure at a constant value, for there is evidence that part of the mercury is removed as a result of polymerisation. To avoid imprisonment¹⁴ of resonance radiation the mercury vapour pressure was not allowed to exceed 0.0003 mm. Another similar reaction vessel completely filled with silica tubes, their axes being set parallel to that of the reaction tube, was employed for experiments on the effect of the proximity of surfaces on the rate of polymerisation. The reaction bulb was placed in a furnace for experiments above 20° and a silica lens projected an approximately parallel beam of light into the reaction tube.

Deposition of polymer on the walls of the reaction vessel cuts down the intensity of light entering the gas and therefore measurements were restricted to low pressures (< 10 mm.) to avoid large corrections on account of this factor. Pressures were measured by a McLeod and a Bourdon gauge. Acetylene was taken from a cylinder and passed slowly through a trap at - 80° in order to remove the greater part of the accompanying acetone. The gas was then subjected to repeated fractionation *in vacuo*, the first fractions only being retained. Ethylene from a cylinder was first passed over P_2O_5 and then fractionally distilled in the same manner as acetylene.

Results.

Effect of Mercury Vapour Pressure.

Preliminary experiments were made with a 100 c.c. bulb attached to a mercury reservoir by a 1 mm. capillary 30 cm. long, no circulating pump being employed. With this arrangement the pressure-time curves consistently exhibited an initial rapid decrease, thereafter the reaction proceeds smoothly as is shown by curves I and II in Fig. 1. Further repeated fractionation of the acetylene failed to remove the abnormality. It was not due to oxygen, for when 10 per cent. O_2 were added the pressure-time curve assumes the shape shown by curve III. Acetylene was polymerised in the bulb and after the initial fast rate of reaction was completed, a further dose of acetylene was admitted; the rapid initial rate was once more obtained. The falling off in rate might be due to an inhibitor. 0.85 mm. of acetylene were admitted, 0.60 mm. being polymerised (curve I). The acetylene was then withdrawn from the insulation vessel which was pumped out. Next the acetylene was condensed into a liquid air trap and subsequently allowed to evaporate slowly into the reaction vessel, the final portion being retained. On switching on the light, however, the initial rapid rate was once more observed (curve II). Finally the mercury vapour pressure was increased to 0.001 mm. when an immediate increase in velocity of polymerisation occurred (curve IV). A similar rapid decrease

¹³ Melville, *J. Chem. Soc.*, 1934, 1244.

¹⁴ Melville, *Proc. Roy. Soc.*, *in the press*.

in rate also obtains with high mercury vapour pressures. These observations suggest that the falling off in rate is due to a diminution of mercury vapour pressure as a result of chemical participation of mercury atoms in the polymerisation reaction. An adequate supply of mercury vapour to maintain the velocity is prevented by the narrow capillary. On putting into operation a reaction system in which the mercury reservoir was close to the insulation tube, the initial kink in the pressure-time curves completely disappeared, thus supporting the indirect evidence obtained above (curves V, VI, VII). This is the reason for utilising a circulatory system when the reaction tube is in a furnace and the mercury reservoir is necessarily at some distance from the zone of reaction.

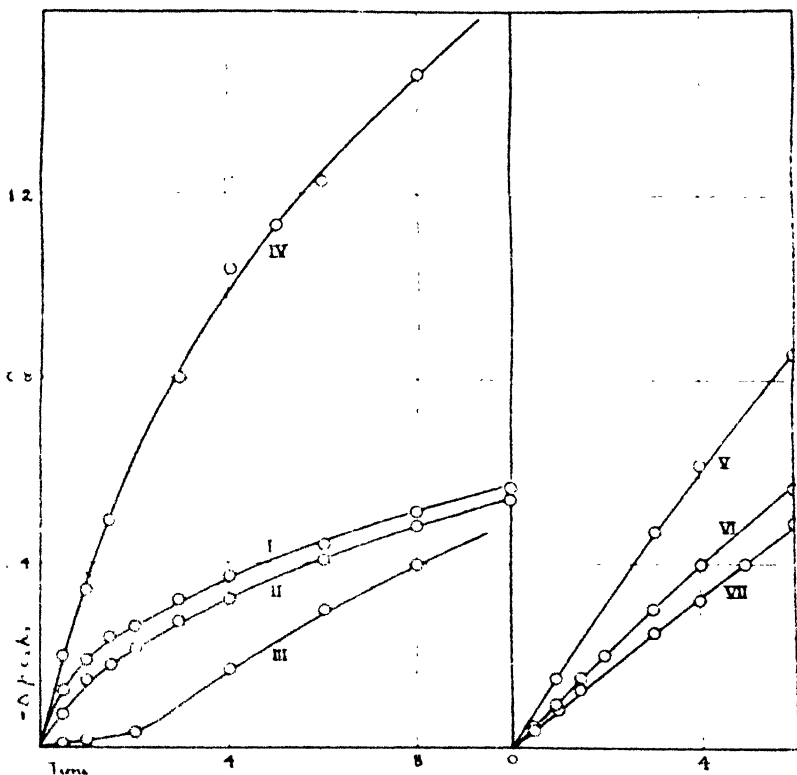


Fig. 1

The conclusion is therefore that mercury atoms are removed during the mercury sensitised polymerisation of acetylene. It is probable that an excited atom on colliding with acetylene forms a complex of the acetylide type which initiates the polymerisation reaction.

Effect of Acetylene Pressure.

At the comparatively low pressures at which these measurements are made, an appreciable fraction of the excited mercury atoms radiate and hence the rate of polymerisation will decrease with diminishing pressure due to this factor alone. Any additional variation, on account of factors operative in the polymerisation itself, will therefore be superposed on processes connected with mercury atoms. The rate of polymerisation may therefore be represented by

$$-\frac{d[C_2H_2]}{dt} = f(P) \cdot k[Hg^*][C_2H_2].$$

where $f(P)$ is that part of the polymerisation process subsequent to the collision of the mercury atom and acetylene molecule. This equation, on allowing for radiation of mercury atoms, becomes

$$-\frac{d[C_2H_2]}{dt} = f(P) \cdot K \cdot \frac{k[C_2H_2]}{k[C_2H_2] + 1/\tau},$$

where K is a constant depending on the light intensity and on the mercury vapour pressure. τ is the life-time (10^{-7} secs.) of the excited atom. The variation of rate from a pressure of 0.01 to 10 mm. is shown in Fig. 2.

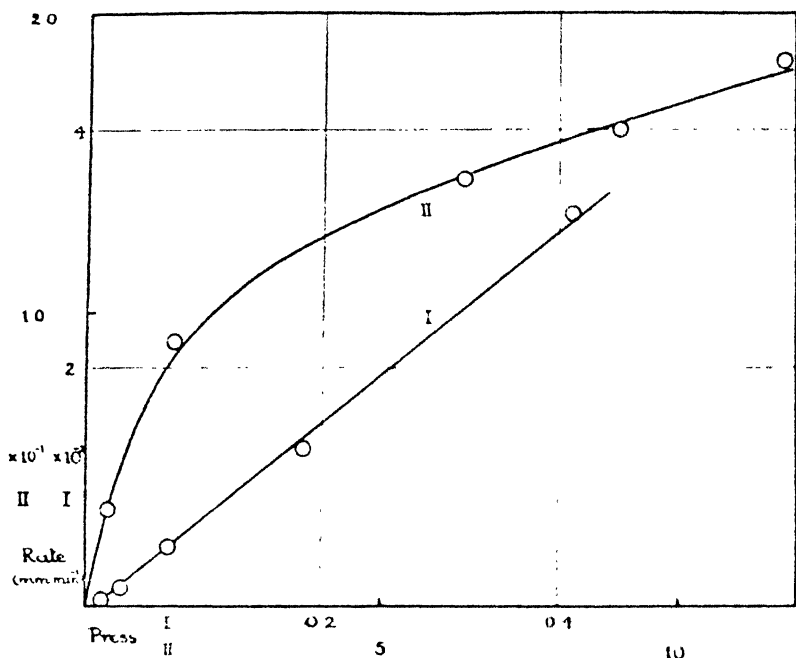


Fig 2

Up to about 0.5 mm. the rate increases with the first power of the pressure. At higher pressures the curve begins to bend round, apparently approaching a maximum. This is better shown by Fig. 3 where the reciprocal rate is plotted against reciprocal pressure giving a linear relation. These are, however, just the relationships to be expected if the factor, $f(P)$, in the above equation is independent of acetylene pressure. The growth and the cessation of growth must therefore be independent of acetylene pressure.

Effect of Temperature.

The following results were obtained at different temperatures (Table I.) where it will be seen that the rate of polymerisation increases to a flat maximum, thereafter decreasing. Above 500° the polymer begins to decompose with the production of hydrogen so that measurements cannot be reliably made. Below 500° polymerisation is unaccompanied by appreciable decomposition and there is no hydrogen or methane produced during polymerisation. Nor was there any formation of measurable quantities of substances less volatile than acetylene, such as benzene. Pressures were adjusted to give constant concentrations of acetylene in the

TABLE I.

Empty Tube. Diameter 5 cm.

Press.	1.21	1.72	2.28	2.97	3.08	3.45	3.48
Temp.	30	99	209	297	355	439	528
Rate (mm./min.)	0.004	0.050	0.090	0.088	0.075	0.070	0.070
Rate/press. rel. to 30° . .	1	8.8	12.7	9.0	7.5	6.2	5.3

Packed Tube. 0.7 cm. Internal Diameter Tubes.

Press	1.30	2.02	2.23	2.54	2.61	3.47	4.00
Temp.	27	110	194	247	297	400	495
Rate (mm./min.)	0.004	0.023	0.044	0.090	0.075	0.09	0.130
Rate/press. rel. to 27 . .	1	3.9	6.8	12.0	10.0	9.0	11.0

reaction bulb. The increase in reaction rate is not due to any increase in the efficiency of collisions of excited mercury atoms with acetylene, for such efficiencies are known to be practically independent of temperature.¹³

Effect of Surfaces.

The experiments in Table I show that so far as the relative rates compared to 27 are concerned, the effect of packing the reaction tube is small. The effect of packing was further investigated at 20 at higher intensities. For example in one set of experiments with an initial pres-

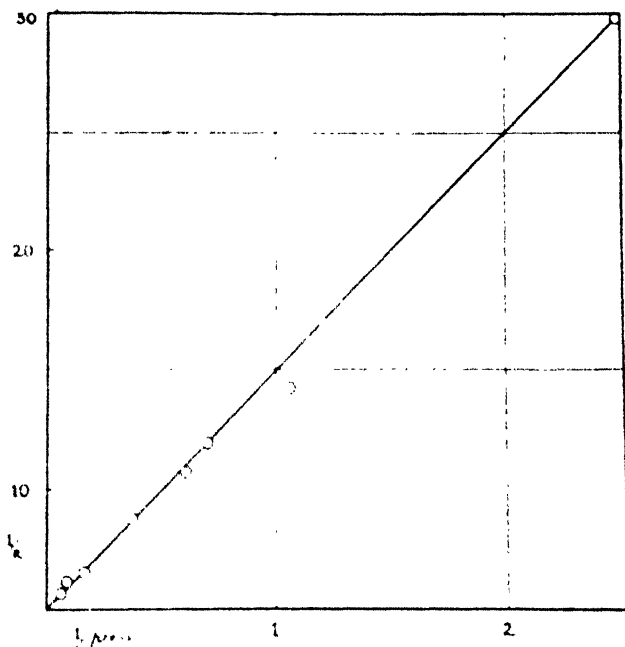


Fig 3

sure of 4 mm., the rate in the empty tube was 0.007 mm./min. and in the packed tube 0.050 mm./min. Fig. 4 shows a complete series of experiments at different pressures and at a temperature corresponding to the maximum rate at which polymerisation occurs. First it will be seen that the rate in the empty tube is on the average 1.6 times faster than in the packed tube. The two lines labelled bimolecular and unimolecular indicate how the rate of polymerisation would vary if it were respectively bi- and unimolecular. The close parallelism of the results to the unimolecular line is in agreement with the data at 20° (p. 262) at lower values of the chain length. At pressures less than 0.05 mm. in the packed tube and to a less extent in the empty tube appreciable thermal decomposition of the

¹³ Cf. e.g. Cario and Franck, *Z. Physik*, 1926, **37**, 619.

polymer occurred with the production of hydrogen and methane, so that reliable measurements of the effect of pressure on the polymerisation could not be made.

Though the polymer is deposited on the walls, the walls do not retard nor accelerate its growth once that is started by excited mercury atoms. Had the chains been stopped at the surface the decrease in rate on packing the vessel would have been $(5/0.7)^2 = 50$ times.

Effect of Intensity.

For this purpose two lamps were arranged to illuminate the same part of the reaction tube at about equal intensities. Three runs were made: (a) lamp 1, (b) lamps 1 and 2, (c) lamp 2. In Table II. two experi-

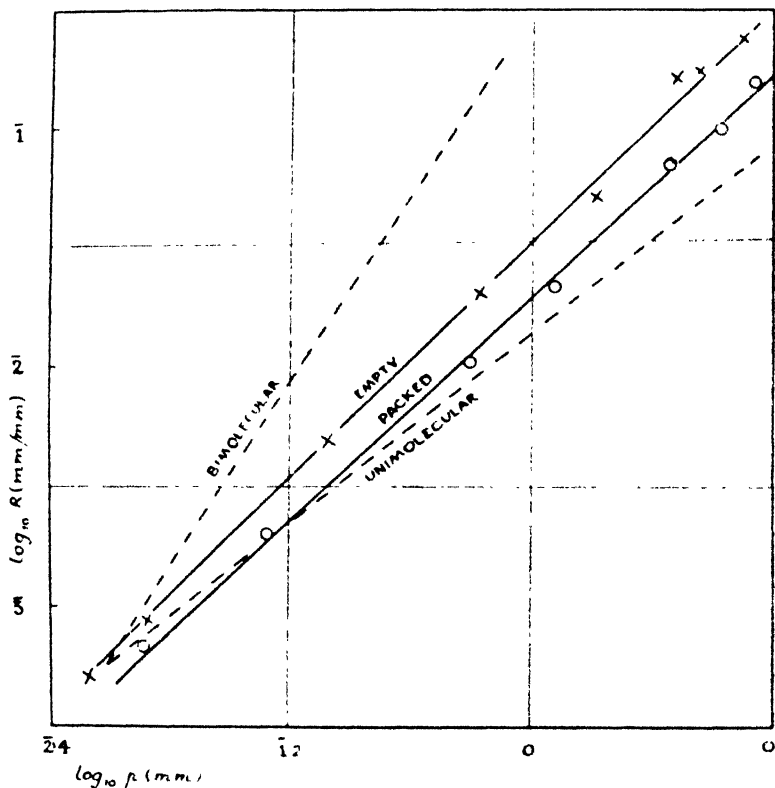


Fig. 4

ments, one at high and the other low pressure, are given to show that the rate of polymerisation due to both lamps operating simultaneously is nearly equal to that when operated separately. This means that the rate of polymerisation is proportional to the rate at which the chains are started.

The Propagation of the Polymerisation in Space.

The polymer may easily be rendered visible by gentle heating *in vacuo* when it carbonises to a darker deposit, thereby fulfilling a useful purpose. Whereas the temperature coefficient of the rate of polymerisation might be able to yield an approximate estimate of the efficiency of the reactions involved, there is a complication in that it is a composite coefficient describing both propagation and termination reactions. An alternative method

TABLE II.

Low Pressure. 0.150 mm.*High Pressure.* 2.98 mm.

Time min.	Pressure of Acetylene Polymerised.				Time min.	Pressure of Acetylene Polymerised.			
	1.	2.	1 + 2 Simul.	1 + 2 Separate.		1.	2.	1 + 2 Simul.	1 + 2 Separate.
2	0.0050	0.0120	0.0150	0.0170	0.5	0.05	0.06	0.17	0.11
4	0.0090	0.0235	0.0320	0.0325	1.0	0.09	0.17	0.25	0.26
6	0.0130	0.0370	0.0470	0.0500	1.5	0.16	0.21	0.34	0.37
8	0.0170	0.0470	0.0605	0.0640	2	0.22	0.24	0.38	0.46
10	0.0200	0.0580	0.0740	0.0780	4	0.39	0.45	0.69	0.74
					6	0.55	0.61	1.00	1.06

of measuring the efficiency of the propagation reaction was therefore necessary. The following device was adopted. A clean cylindrical reaction vessel 5 cm. long and 5 cm. in diameter was fitted with a band of tin foil 1 cm. wide around the middle (Fig. 5). The mercury vapour pressure was raised to 0.001 mm. so that 50 per cent. of the resonance light was absorbed in penetrating through 2 mm. of vapour, the zone of initiation of the polymerisation being thereby confined to a region close to the walls. The mercury lamp was placed about 10 cm. from the reaction vessel opposite the foil. On carrying out the polymerisation at high pressure—10 mm.—it was observed that only the side of the reaction vessel facing the lamp became covered with polymer. The zone of reaction

must then be confined to a region close to the wall—an observation further supported by the fact that there was no visible trace of the deposit behind the tin foil. This was most easily observed by heating the whole of the bulb to carbonise the deposit, admitting oxygen and applying a fine pointed flame along a line parallel to the axis of the tube (Fig. 5a). A small portion of the wall was thus cleared of polymer in order to serve as a control in visually estimating the density of deposit. As the pressure is lowered the zone of initiation remains the same, but the zone of polymerisation will

extend further into the bulb. At 6.71 mm., 1.35 mm. of acetylene being polymerised, no visible trace of the deposit could be detected at more than 1 mm. from the edge of the foil. On reducing the pressure to 0.9 mm., depositing 2 mm. of acetylene in successive runs, the deposit had crept distinctly behind the foil, but the middle point was still clear of polymer (Fig. 5b). Finally at 0.1 mm. the deposit appeared to be fairly evenly distributed behind the foil (Fig. 5c), although the density of deposit was not so great as that on the parts of the bulb directly exposed to the lamp. At a pressure of 1 mm. therefore the building up of the polymer occurs during a time in which the chain has diffused a distance of a few millimetres. A molecule of normal dimensions will diffuse through

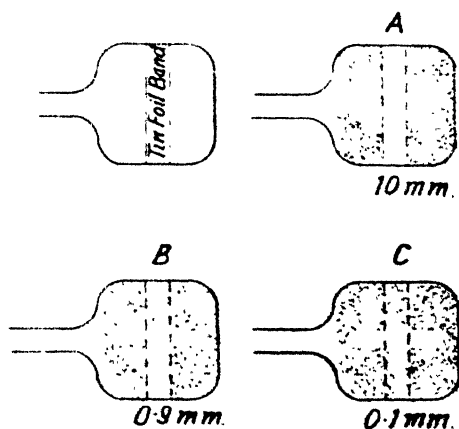


FIG. 5

a layer of 1 cm. of acetylene at 1 mm. pressure in about 10^{-3} sec., during which it experiences about 10^4 collisions. If the chain length is 10, reaction occurs once in every 10^3 collisions, which in turn corresponds to an average energy of activation of 4000 cal., if only two square terms were involved.

This shadow method can also be applied to the question whether polymer is selectively deposited on a surface already covered. Starting with a clean bulb having the strip in position, about 0.010 mm. of acetylene were polymerised. The strip was then removed and 2 mm. of C_2H_4 polymerised at a pressure of 6 mm. On carbonisation no selective deposition of the polymer could be observed.

Ethylene.

A number of experiments were also made with ethylene. They serve to demonstrate that the polymerisation of this molecule occurs by rather an indirect mechanism. In agreement with preliminary experiments of Olson and Meyers¹¹ it was observed that on first illuminating ethylene at 20° there was a marked *increase* in pressure, followed later by a decrease, there being a residual pressure on prolonged exposure. The initial increase becomes more predominant as the pressure of ethylene is lowered, and for a given intensity of light the maximum is reached more quickly at low pressures. The following figures show the magnitude of these effects:—

Press. of C_2H_4 . . .	9.88	6.83	4.65	2.36	1.61	0.19	0.11	0.003
Max. increase in tot. press. . .	0.63	0.41	0.35	0.10	0.22	0.041	0.041	0.024
Max. increase C_2H_4 .	0.064	0.060	0.076	0.081	0.136	0.215	0.28	0.38
Time for increase (min.) . .	10	9	6	5	2.5	18	15	20

The increase is due to the production of gas non-condensable in liquid air. Since the pressure of gas condensable in liquid air remains constant the non-condensable gas must be hydrogen. The ethylene then is first dissociated into hydrogen and acetylene. The latter will polymerise as described in the previous pages. The hydrogen pressure does not continue to rise but gradually reaches a maximum, as is shown by Fig. 6. Here the results of a series of experiments starting with identical C_2H_4 concentrations have been plotted to indicate the total pressure, pressure of hydrogen and of condensable gas. The hydrogen must be consumed in the hydrogenation of the acetylene polymer since the decrease in total pressure shows that ethane, arising out of the hydrogenation of ethylene by atomic hydrogen, cannot be a final product of the reaction. Making the assumption that after the maximum in the total pressure time curve is attained, the acetylene and hydrogen disappear in equimolecular amounts, it then becomes possible to plot on the same diagram the pressure of ethylene and of acetylene during the whole course of polymerisation. The final ethylene polymer may thus be regarded as a hydrogenated polymer of acetylene. The polymerisation of ethylene is therefore not a chain reaction like that of acetylene because every molecule polymerised must first have been dissociated by a collision with an excited mercury atom. The difference between the acetylene and ethylene reactions is further emphasised when their temperature coefficients are compared. The rate of ethylene polymerisation is practically unaffected by raising the temperature from 27° to 280°, compared with an approximately 10-fold increase with acetylene. For example, at 2.01 mm. C_2H_4 and 27° the rate of the initial increase of pressure was 0.08 mm. per min. and at 280° at a pressure of 4.13 mm., 0.07 mm./min. It is noteworthy that even at elevated

temperatures the molecule which initiates polymerisation of acetylene does not induce the polymerisation of ethylene, which is not surprising having regard to the fact that ethylene itself only forms a dimer at higher temperatures, whereas acetylene polymerises to a variety of products.

The behaviour of acetylene may be briefly recapitulated :

(1) Acetylene is polymerised at 20°C . to a substance whose formula is approximately $(\text{C}_2\text{H}_2)_n$ by ultraviolet light, excited mercury atoms and α -particles. Each type of stimulus induces the reaction of several molecules of acetylene.

(2) The chain length (ν) is independent of pressure from 0.1 to 760 mm., independent of the rate at which chains are started and independent of the diameter of the reaction tube.

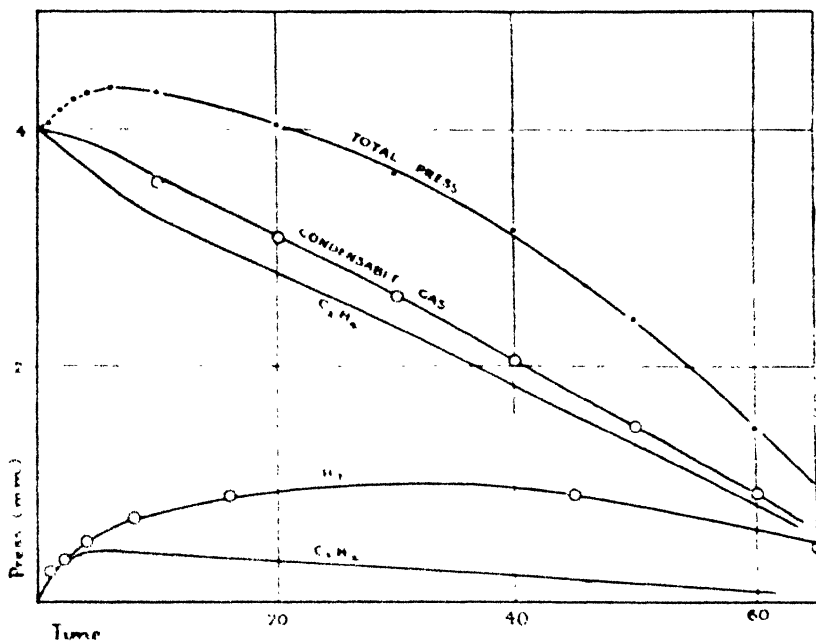


FIG. 6.

(3) ν increases from about 10 at 20° to about 100 at 250° , at which temperature it is a maximum and tends to decrease above 250° . The initial increase in ν with temperature corresponds to an energy of activation of 4000 cal.

(4) By measuring the distance of propagation of the chains in space, the average energy of activation for propagation amounts to not more than 4000 cal.

The Mechanism of the Reaction.

Since the reaction is of the chain type in the sense that one activated molecule of acetylene may induce the reaction of several others, the polymer must in the first instance be built up by the successive addition of acetylene molecules. The molecular weight of the polymer ought therefore to be equal to the chain length multiplied by the molecular weight of acetylene. At 20° the chain length is 10 and the empirical

formula should be $(C_2H_2)_{10}$. Hydrocarbons containing 20 carbon atoms are volatile on heating to 200-300° in a high vacuum. The acetylene, however, partly decomposes when attempts are made to sublime it. This would appear to suggest that there is some secondary polymerisation of the products of the gaseous chain reaction.

The chain length is finite and therefore a reaction must come into play which prevents further addition of acetylene molecules. There are three types of collision which might be responsible for this phenomenon. (1) Two polymers mutually destroy each other in so far as further addition of acetylene is concerned. (2) A collision between an acetylene molecule and the polymer, of a different character to the propagating collision, deactivates the latter. (3) The chain carrying polymer is spontaneously deactivated. Deactivation cannot occur at the walls since packing the reaction vessel does not diminish the chain length.

The consequences of the second type of collision may now be considered in order to show how it is possible to treat the problem of polymerisation by the principles of chemical kinetics. To obtain the rate of polymerisation the concentration of each of the transitorily occurring polymers must be known and in addition their velocity coefficients of reaction with acetylene. Fortunately a certain amount of simplification arises automatically. Let $I[C_2H_2]$ be the rate at which acetylene molecules are activated, the activated molecules being denoted by $[C_2H_2]_1$. $k_1[C_2H_2]_1[C_2H_2]$ is the rate at which acetylene molecules add on to activated acetylene and $k'_1[C_2H_2]_1[C_2H_2]$ the rate at which such molecules are deactivated. Then for each polymer molecule there will be a stationary state equation

$$\frac{d[C_2H_2]_1}{dt} = I[C_2H_2] - k_1[C_2H_2]_1[C_2H_2] - k'_1[C_2H_2]_1[C_2H_2] = 0.$$

$$\frac{d[C_2H_2]_2}{dt} = k_1[C_2H_2]_1[C_2H_2] - k_2[C_2H_2]_2[C_2H_2] - k'_2[C_2H_2]_2[C_2H_2] = 0,$$

$$\frac{d[C_2H_2]_n}{dt} = k_{n-1}[C_2H_2]_{n-1}[C_2H_2] - k_n[C_2H_2]_n[C_2H_2] - k'_n[C_2H_2]_n[C_2H_2] = 0.$$

Adding these equations,

$$I[C_2H_2] = k_n[C_2H_2]_n[C_2H_2] + \{k'_n[C_2H_2]_n + k'_{n-1}[C_2H_2]_{n-1} + \dots + k'_1[C_2H_2]_1\}[C_2H_2],$$

$$I = k_n[C_2H_2]_n + \{k'_n[C_2H_2]_n + \dots + k'_1[C_2H_2]_1\}.$$

Solving each equation for the value of $[C_2H_2]_n$,

$$[C_2H_2]_1 = \frac{I[C_2H_2]}{k_1[C_2H_2] + k'_1[C_2H_2]} = \frac{I}{k_1 + k'_1},$$

$$[C_2H_2]_2 = \frac{k_1[C_2H_2]_1[C_2H_2]}{k_2[C_2H_2] + k'_2[C_2H_2]} = \frac{k_1}{k_2 + k'_2} \cdot \frac{I}{k_1 + k'_1},$$

$$[C_2H_2]_3 = \frac{I}{k_1 + k'_1} \cdot \frac{k_1}{k_2 + k'_2} \cdot \frac{k_2}{k_3 + k'_3},$$

$$\dots$$

$$[C_2H_2]_n = \frac{I}{k_1 + k'_1} \cdot k_1 \dots \frac{k_{n-1}}{k_n + k'_n}.$$

Hence

$$-\frac{d[\text{C}_2\text{H}_2]}{dt} = I[\text{C}_2\text{H}_2] + [\text{C}_2\text{H}_2][\text{C}_2\text{H}_{2,1}\{k_1 + k'_1\} \\ + [\text{C}_2\text{H}_2][\text{C}_2\text{H}_{2,2}\{k_2 + k'_2\} + \dots + [\text{C}_2\text{H}_2][\text{C}_2\text{H}_{2,n}\{k_n + k'_n\}.$$

Whence, substituting for the values of $[\text{C}_2\text{H}_{2,n}]$,

$$-\frac{d[\text{C}_2\text{H}_2]}{dt} = [\text{C}_2\text{H}_2] \left\{ 2I + \frac{I}{k_1 + k'_1} \cdot k_1 + \dots \right. \\ \left. + \frac{I}{k_1 + k'_1} \cdot \dots \cdot \frac{k_{n-1}}{k_n + k'_n} (k_n + k'_n) \right\}, \\ \nu = -\frac{d[\text{C}_2\text{H}_2]/dt}{I[\text{C}_2\text{H}_2]} = 1 + \left\{ 1 + \frac{k_1}{k_1 + k'_1} + \dots \right. \\ \left. + \frac{k_1}{k_1 + k'_1} \cdot \frac{k_2}{k_2 + k'_2} \cdot \dots \cdot \frac{k_{n-1}}{k_{n-1} + k'_{n-1}} \right\}. \quad (\text{A})$$

or generally

$$\nu = \sum_0^{n-1} \{ (1 + k''/k) \}^{-1} + 2.$$

If the chain stops by the spontaneous decomposition of the polymer molecule, the last term in the equation for the stationary concentration of the various carriers becomes $k_1''[\text{C}_2\text{H}_{2,1}][\text{C}_2\text{H}_2]$, etc. Proceeding in the same way it may be shown that

$$\nu = 1 + \{ 1 + k_1''/k_1[\text{C}_2\text{H}_2] \}^{-1} + \dots \\ + \{ 1 + k_1''/k_1[\text{C}_2\text{H}_2] \}^{-1} \cdot \dots \cdot \{ 1 + k_n''/k_n[\text{C}_2\text{H}_2] \}^{-1},$$

$$\text{or} \quad \nu = \sum_0^n \{ (1 + k''/k[\text{C}_2\text{H}_2]) \}^{-1} + 1,$$

and hence ν will be proportional to the acetylene pressure.

Finally consideration of the mutual destruction of the polymer carriers gives an equation showing that the chain length is a function of the rate of starting and of the acetylene pressure. The experimental data definitely support the first mechanism, that is, termination occurs in a collision between a growing polymer and acetylene, for ν is independent of $[\text{C}_2\text{H}_2]$ and of I . But this is also the propagating type of collision and therefore there must be two kinds of collision—one for propagating the growth of the polymer and the other for stopping it. The next question is to separate the two types.

As a first approximation it will be assumed that $k'_1/k_1 = k'_2/k_2 = x$. Equation (A) becomes

$$\nu = 1 + \left(1 + \frac{1}{1+x} + \frac{1}{(1+x)^2} + \dots \right).$$

If x is not too small this series converges rapidly and summing to ∞ terms,

$$\nu = 2 + 1/x.$$

x cannot be unity, for ν is greater than 3. If the chains are long,

$$\nu = k/k' = \alpha/\alpha', \quad e = (E - E')/RT,$$

where α and α' are coefficients incorporating steric factors and square terms (if more than two square terms are involved in the collisions). At 20° , $\nu = 10$ and $E - E' = 4000$ cal. α/α' is then 8×10^3 . Considering the steric factor first, it is probable that only a small portion of the polymer molecule has the property of adding on an acetylene molecule. On the other hand, two possibilities may be distinguished in the termination collisions. (a) The acetylene molecule on colliding with the polymer disintegrates it into fragments incapable of further propagating the chain (steric factor large compared with that in propagating collision). (b) The acetylene molecule becomes attached to that position at which growth of the polymer normally occurs, but a rearrangement of bonds takes place such as to prevent the further addition of acetylene (steric factors for propagation and termination equal). If steric factors alone controlled the magnitude of α/α' then α' would be equal to or greater than α . The factor expressing the increased rate of activation due to the participation of more than two square terms in the activation process is

is $\frac{1}{(s/2 - 1)!} (E/RT)^{s/2 - 1} + \frac{1}{(s/2 - 2)!} (E/RT)^{s/2 - 2}$, since E/RT is not very large,¹⁶ ca. 10. E is greater than E_1 and hence the square term factor for propagation will be greater than the termination factor if $s \geq s'$. If further $s > s'$ then the ratio of propagation to termination factor will decrease with temperature and will therefore tend to compensate for the increase brought about by the simple energy of activation factor $e^{-(E-E')/RT}$, thus making the chain length finally independent of temperature. If x is a function of the size of the polymer, this will make the series expressing the chain length converge more rapidly, but the suggested explanation of the maximum in the chain length—temperature curve remains as before.

According to the treatment given above, the average molecular weight of the polymer will be equal to $\nu \cdot M_{C_2H_2}$, but since there is a finite probability that the chain will be stopped at any link, the molecular weight of the products of the chain reaction will theoretically extend from $1 \cdot M_{C_2H_2}$ to $\infty M_{C_2H_2}$. When x is a function of the size of the polymer, however, the tendency for the formation of polymers of high molecular weight will be curtailed.

Summary.

The mercury photosensitised polymerisation of acetylene has been studied at pressures from 0.05 to 10 mm. and at temperatures from 20° to 500° C. with the following results:

The excited mercury atoms form, with an acetylene molecule, a complex, which then adds on further acetylene molecules thereby producing a polymer by a chain mechanism. The chain length (no. of acetylene molecules polymerised per excited mercury atom deactivated by acetylene) is independent of acetylene pressure, of the rate at which chains are started and is not affected by packing the reaction bulb. The chain length (10 at 20°) increases to 100 at 250° , thereafter decreasing.

These kinetics are shown to be consistent only with the assumption that the cessation of the growth of the polymer is due to a collision of an acetylene molecule with the growing polymer but of a different kind to that responsible for propagation.

Ethylene also polymerises under the same conditions, but it would appear that the first stage is the dissociation to hydrogen and acetylene

¹⁶ Hinshelwood, *Kinetics*, p. 24, 3rd edit.

followed by the polymerisation of acetylene and finally the partial hydrogenation of the acetylene polymer.

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THE POLYMERISATION OF PHOSPHORUS.

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It is generally conceded that, of the two allotropic modifications of phosphorus, the red one is a polymer. How the polymer is constructed and from what size of unit is not very clearly defined in the few papers¹ on the subject. Attempts have been made to measure its molecular weight and it is suggested that this is P_8 or even higher.¹ Much work, too, has been carried out on the conditions necessary for the reversible transformation white \rightleftharpoons red to proceed. In so far as the equilibria of the system are concerned, the position may be regarded as satisfactory in its main outlines.² With regard to the constitution of white phosphorus there is, for the present purpose, not much doubt. It dissolves in solvents such as carbon disulphide in units of P_4 and its vapour density also shows that P_4 molecules are in equilibrium with the solid.

No attempts have, however, been made to elucidate the nature of the transformation nor of the constitution of red phosphorus (if it is a polymer) by the methods of chemical kinetics, probably because the system is not an easy one to work with. The vapour pressures of both modifications are small at $15^\circ C$. and even their ratio at high temperatures is rather high, only attaining equality at the inconvenient pressure of 41 atmospheres.

The present paper therefore describes an attempt to apply kinetic concepts to the problem. During the course of some experiments on the heterogeneous initiation of reaction chains in phosphorus-oxygen mixtures at low pressures by means of a tungsten filament,³ it was frequently observed that the reaction bulb became covered with a film of red phosphorus. It was noteworthy, moreover, that the deposit often appeared at some considerable distance from the zone of reaction, even penetrating into narrow capillaries. Apparently besides catalysing the chain reaction, the tungsten could in some way transform phosphorus-vapour to red phosphorus, for the red deposit is not formed if phosphorus and oxygen are allowed to combine spontaneously at pressures only slightly higher than those employed for the stable chain reaction.

¹ Cf. e.g. Schenck, *Ber.*, 1902, **35**, 351.

² Cf. Findlay, *The Phase Rule*, p. 59, Longmans.

³ Melville and Ludlam, *Proc. Roy. Soc.*, 1932, **A135**, 315.

Similar deposits of red phosphorus, unaccompanied by white phosphorus or phosphorus vapour, are obtained when phosphine is decomposed by light of $\lambda < 2300 \text{ \AA}$,⁴ by excited mercury atoms,⁵ or on the surface of tungsten or molybdenum.⁶ By passing a stream of P_4 molecules through a silica jet at $500\text{--}800^\circ$ in the apparatus shown in Fig. 1. circular deposits of red phosphorus may be collected on a glass surface cooled to -80° and of an area to be expected from the geometry of the jet system. Summarising then, it appeared that if P_4 molecules be heated to a high enough temperature, or if phosphorus be formed in the decomposition of phosphorus containing molecules, it is invariably deposited as the red modification.

At room temperatures, red phosphorus has a negligible vapour pressure and therefore the transformation in presence of a tungsten filament seemed to a comparatively simple type of heterogeneous reaction which might help to throw some light on the manner in which red phosphorus is deposited and also on the constitution of red phosphorus itself.

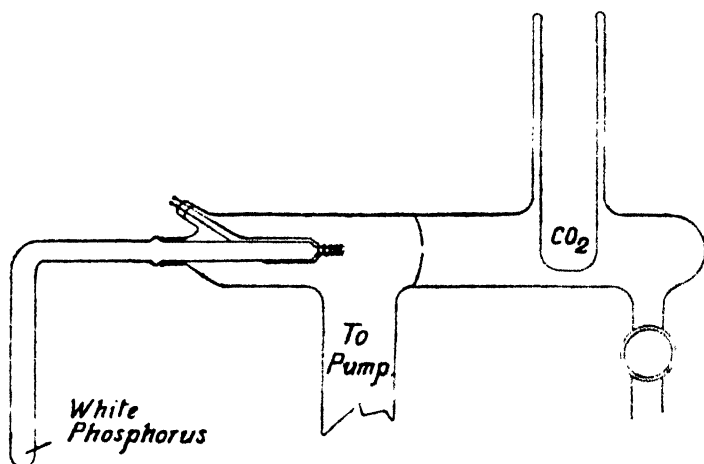


FIG. 1.

Another problem on which a simple heterogeneous reaction of this nature might be able to yield some information is as follows. In certain heterogeneous reactions, the collision efficiency of the reactant molecule happens to be approximately equal to $e^{-E/RT}$ where E is the apparent energy of activation as measured by the temperature coefficient of the reaction velocity.⁷ Such a relationship, though probably fortuitous, would imply that molecules merely collide with the surface, abstract from it an energy equal to or greater than E and react forthwith. If such were the case, molecules possessing in the gas phase energy rather greater than the average would react more readily since they do not need to acquire so much energy from the surface. In other words, the energy of a molecule in the gas may contribute to the energy of activation derived from the surface and so aid its decomposition thereon.

⁴ Melville, *Proc. Roy. Soc.*, 1933, A139, 541.

⁵ *Ibid.*, 1932, A138, 374.

⁶ Melville and Roxburgh, *J. Chem. Soc.*, 1933, 586.

⁷ See e.g., Hinshelwood, *Kinetics*, p. 360.

At high pressures, and with filament catalysts, it is difficult to disentangle such effects because there is a region of gas round the filament at the same temperature as the filament itself. In point of fact, reactions are known⁸ where the decomposition goes on in this gas layer and not upon the surface.

By performing experiments at low pressures, in which the molecules colliding with the filament possess on the average an energy corresponding to the temperature of the containing vessel such information may be obtained by varying the temperature of the reaction bulb, maintaining that of the filament constant. If the rate of reaction remains unchanged, it is certain that all molecules have an equal probability of reacting on the surface those of high energy content not being specially favoured. This would mean that the molecules which react sojourn on the surface at least long enough to come into complete thermal equilibrium with it. Langmuir⁹ with this viewpoint in mind found that bulb temperature had no effect on the rate of attack of tungsten by oxygen to form WO_3 . A similar test may be made with the tungsten-phosphorus system but with the important difference that the tungsten is not attacked.

Anomalies in the Vapour Pressure of Red Phosphorus.

In dealing with the transformation red phosphorus \rightarrow white phosphorus, it has always been assumed that the vapour in equilibrium with both modifications consists of P_4 molecules. If now the thermal relations concerning the reaction be examined a curious anomaly is revealed.

First it is necessary to collect the available somewhat scattered data on vapour pressures. From the experiments of Centnerswer and others¹⁰ it is concluded that vapour pressure of liquid white phosphorus is given by

$$\log_{10} p \text{ (mm.)} = 9.6511 - 3297/T$$

which corresponds to a heat of evaporation of 15.8 kg. cal. per mole. Recalculating the data at 44–150° C., a smaller value of 12.9 kg. cal. is obtained. From the measurements of Smits and co-workers¹¹ on the variation of the vapour pressure of solid red phosphorus with temperature, the mean value obtained for the heat of evaporation is 25.6 kg. cal. The heat of transformation white to red is 4.0 kg. cal.¹² and if a small cycle be set up, it will be seen that there is a discrepancy in the heat content change of the system of 8.9 kg. cal. Admittedly the heat of transformation is not known very accurately, but it is certainly not in error by 8.9 kg. cal., which would be required to make good the discrepancy. Even such an approximate rule as that of Trouton shows that the vapour pressure of red phosphorus is anomalous. White phosphorus has a vapour pressure of 760 mm. at 280.5° C. and therefore Trouton's constant is 23. Red phosphorus has a vapour pressure of 760 mm. at 417.5° C., Trouton's constant being 37.4, compared with an average value of 22. If the hypothesis be made that red phosphorus is in equilibrium,

⁸ Steacie, *J. Physical Chem.*, 1932, **36**, 3074.

⁹ Langmuir, *J. Amer. Chem. Soc.*, 1913, **35**, 105.

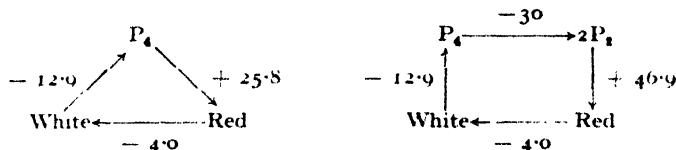
¹⁰ Centnerswer, *Z. physik. Chem.*, 1913, **85**, 99; Preuner and Brockmoller, *ibid.*, 1912, **81**, 129; MacRae and van Voorhis, *J. Amer. Chem. Soc.*, 1921, **43**, 547.

¹¹ Smits and co-workers, *Z. physik. Chem.*, 1914, **88**, 608; 1915, **90**, 129; 1916, **91**, 249.

¹² Giran, *Comp. Rendus*, 1903, **136**, 550, 677.

not with P_4 molecules, but with P_2 molecules, the anomaly may be removed to a large extent.

The cycle of processes is therefore amended to that shown



The energy of dissociation $P_4 \rightarrow 2P_2$ has been taken as 30 kg. cal.¹³ and hence the energy required to evaporate two moles of P_2 is 46.9 or 23.9 cal. per mole. Other measurements have indicated the dissociation energy to be rather larger, namely 50 kg. cal. per mole,¹⁴ from which the heat of evaporation turns out to be 33.5 kg. cal.

When red phosphorus is heated in an enclosure in order to determine its vapour pressure, P_2 molecules evaporate and condense. In the gas they combine partly to form P_4 , the equilibrium $[P_2]^2 = K [P_4]$ being established. The measured vapour pressure is that due to P_4 and P_2 molecules and therefore is not a true indication since the equilibrium is almost wholly on the P_4 side, at low temperatures. The observed vapour density in fact shows this to be the case and naturally it would be concluded that P_4 molecules are in equilibrium with red phosphorus. The concentration of P_4 molecules over red phosphorus is then given by

$$[P_4] = [P_2]^2/K \cdot \exp. (-2\lambda_{P_2}/RT + E_{P_4 \rightarrow 2P_2}/RT) \sim e^{-\lambda_{R.P.}/RT},$$

where λ_{P_2} and $\lambda_{R.P.}$ are the true and apparent heats of evaporation of the red modification. From the observed vapour pressures

$$E_{P_4 \rightarrow 2P_2} - 2\lambda_{P_2} = -25.8,$$

$$\text{therefore if } E_{P_4 \rightarrow 2P_2} \text{ is } 30.0, \quad \lambda_{P_2} = 27.9,$$

$$\text{and if } E_{P_4 \rightarrow 2P_2} \text{ is } 50.0, \quad \lambda_{P_2} = 37.9.$$

The first value is in good agreement with that calculated from the second cycle of processes. The second is definitely too high. The uncertain value of the energy of transformation may be the cause of the discrepancy—a higher value would be required to obtain better concordance. It so happens, if $E_{P_4 \rightarrow 2P_2}$ is 30.0 kg. cal., the temperature coefficient of the pressure of P_4 and P_2 above red phosphorus gives an apparent heat of evaporation not far removed from the true value. The real vapour pressure will, however, be very much smaller than that observed.

If this argument be correct, it suggests a mechanism whereby P_4 molecules may form red phosphorus and therefore how the transformation may proceed via the gas phase. The essential condition is that the phosphorus molecule— P_4 —be dissociated to P_2 which must impinge on a surface before recombination in the gas can occur. Conversely, if red phosphorus be deposited as a result, say of the decomposition of phosphine, it would be inferred that P_2 molecules were formed in the penultimate stage of the decomposition.

Experimental.

The principle of the method employed in these experiments was simple. Phosphorus vapour from white phosphorus was admitted to a suitable

¹³ Preuner and Brockmüller, *Z. physik. Chem.*, 1912, **81**, 129.

¹⁴ Stock and Stamm, *Ber.*, 1913, **46**, 3497.

reaction bulb fitted with a tungsten filament and the 'clean up' followed by a Pirani gauge.

The white phosphorus was made in the following way. Red phosphorus was suspended in a hot solution of sodium hydroxide to free it from oxide. It was then washed, dried and sealed into the apparatus. It was at first heated gently in a good vacuum to remove all traces of water vapour and of oxide and then heated more strongly to obtain white phosphorus. The phosphorus reservoir was finally opened to the pumps for several hours and an appreciable fraction of white phosphorus evaporated in order to be absolutely certain that all traces of volatile oxides were removed. The vapour pressure was regulated by immersing the reservoir in a vacuum flask containing water or ice at the required temperature.

The Pirani gauge was fitted with a platinum filament 0.01 mm in diameter maintained at about 100° C., at which temperature the phosphorus vapour did not appear to attack the metal. The gauge was used by reading the voltage required to maintain the bridge circuit balanced, in which case the relationship

$$\frac{V^2}{1 + \frac{V^2}{V_0^2}} = kp$$

(where V_0 and V are the balancing voltages for pressures zero and p) holds valid up to pressures higher than those encountered in these experiments. Calibration was effected by immersing the phosphorus in a water bath at various temperatures and calculating the vapour pressures by extrapolation from measurements made at higher temperatures. This gave a value of k of 181, compared with 122 for oxygen, thus constituting an approximate test of the validity of the extrapolated values of the vapour pressure.

A number of different reaction vessels were employed, each being fitted with a divided filament for more accurate temperature determination, as has previously been described.⁶ The method was however slightly altered. The two filaments were placed in one arm of the bridge and a high resistance voltmeter used for measuring the voltage drop across each filament. The total resistance of the two was known from the bridge resistances so the resistance of each could be calculated. A variable resistance could be inserted in place of the longer filament when measuring the contribution made by the shorter filament to the total reaction velocity. An accurate ammeter was also inserted in the bridge circuit so that the watts input to the filaments could be determined at any instant during the reaction. The filaments were thoroughly outgassed before use and the resistance temperature curve of the tungsten measured by separate experiments.

The reaction bulbs were cleaned with bromine water to remove red phosphorus, rinsed with distilled water and finally baked in vacuo at 350° C. for several hours. Temperature was controlled by immersion in a large vacuum flask containing water. Reaction vessel I (Fig. 2) was cylindrical, 2 cm. in diameter and had a volume including connections of 157 cc. Dimensions of filaments were 12 and 3 cm. long, 0.1 mm. in diameter. Reaction II was a bulb of about 5000 cc., fitted with short and thin filaments, the dimensions being so arranged that if every molecule striking the filaments reacts the half life is about 60 sec., if the reaction is unimolecular. By means of a ground joint and a small windlass a glass cylinder, 1 cm. in diameter, could be lowered to surround both filaments. In this way the red phosphorus could be collected before reaching the walls of the large bulb. Reaction vessel III was of similar external dimensions to I except that it was fitted with a single filament only. This was surrounded by a pyrex cylinder wound with nichrome strip which in turn was covered with another closely fitting cylinder. A Pt-Pt-Pd thermocouple in a thin pyrex sheath measured the temperature of the surface of the inner cylinder. The whole could be immersed in a bath of a CO₂-ether mixture at -80° C. Reaction vessel IV consisted essentially of a plate P upon

which red phosphorus could be deposited by means of a moveable filament system not shown in the diagram. Above P there was a liquid air cooled surface L, and below a furnace F consisting of several spirals of tungsten backed by a nickel reflect or in order to heat P by radiation. Full details

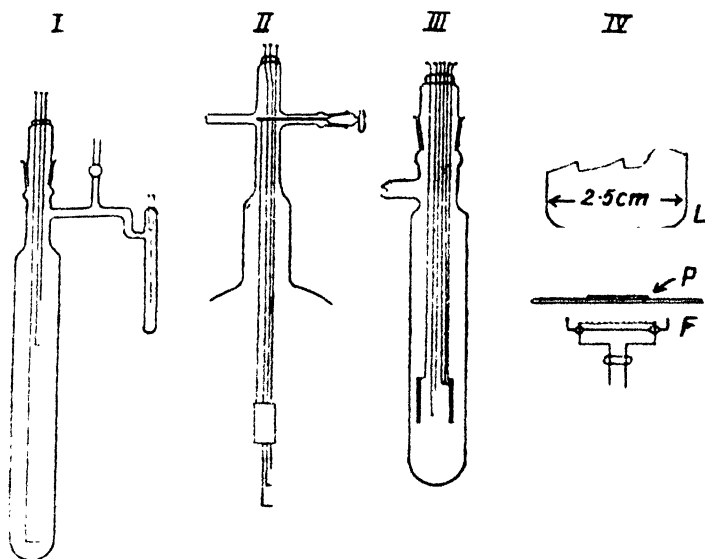


FIG. 2.

of this tube will be published later. Reaction vessel V was again similar to I, but a single short filament was placed at the bottom of the tube; in some experiments to be described below a mica disc was suspended in the middle of the tube. Arrangements were also made for heating various parts of the tube by means of a moveable furnace.

Results and Discussion.

A few typical runs with reaction vessel I (R.V. I.) showed that the phosphorus deposited readily as the red modification and approximately

TABLE I. R.V. I. TEMP. 15°C

Initial Pressure mm.	Initial Rate mm. min. $\times 10^4$.	$t_{\frac{1}{2}}$ min.	Filament Temperature $^{\circ}\text{C}$.	Efficiency * (e).
0.0186	40.0	1.8	535	7.2×10^{-4}
0.0186	51.5	2.0	535	5.0×10^{-4}
0.0188	8.9	14.4	532	9.1×10^{-5}
0.0188	1.4	—	530	—
0.0188	1.7	—	555	—
0.0181	4.7	28.4	508	5.8×10^{-5}
0.0178	12.6	8.2	508	1.59×10^{-4}

* For calculation see text.

From the dimensions of the apparatus, the fraction of molecules reacting to those striking the filament has been calculated, the assumption being made that every molecule activated by the filament is deposited

according to a unimolecular mechanism as may be seen from Fig. 3 where $\log_{10} p_0/p$ is plotted against t . p_0 is the initial pressure of P_4 and p that after time t . Table I gives a series of runs carried out at different temperatures.

as the red modification and is not transformed back to P_4 in the gas or at the walls. The temperature coefficient of this fraction yields an apparent energy of activation of 41 kg. cal. The red phosphorus was fairly uniformly deposited on the surface of the bulb but there was visible evidence that during some runs certain portions of the surface collected more red phosphorus than others. In addition, red phosphorus gradually made its way into other parts of the apparatus.

On account of the selective deposition of red phosphorus and also having re-

gard to the belief that the red modification is some kind of polymer, it appeared that the condition of the surface controlled the effectiveness of the encounters with the walls. In addition, the stream density of active molecules might also determine whether red phosphorus would be deposited at all. Some early preliminary experiments indicated that towards the end—90 per cent of P_4 cleaned up—the reaction came to a stop, the pressure

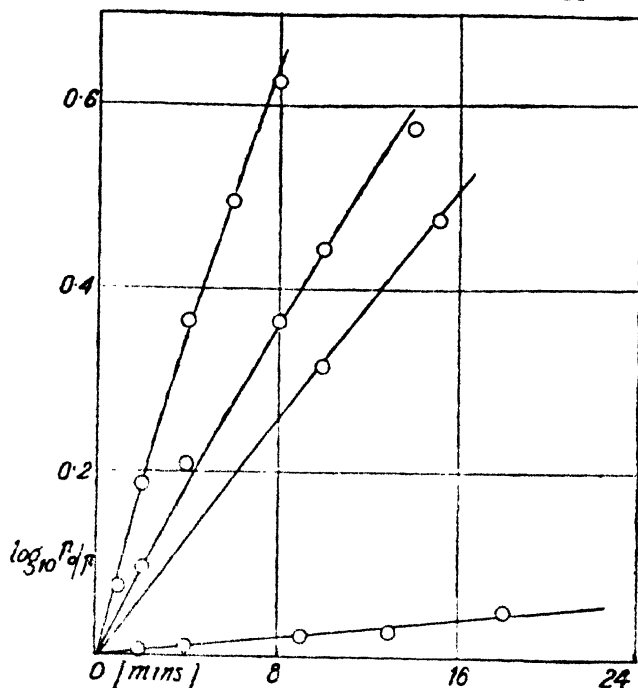


FIG. 3.

TABLE II R.V. II Vol 5460 CC. EFFECTIVE AREA OF FILAMENT 1.68 CM.²

Temperature 1540°			Temperature 1550°		
Time Min.	P_{P_4} Sheath On.	P_{P_4} Sheath Off	Time min.	P_{P_4} Sheath On.	P_{P_4} Sheath Off.
0	0.0186	0.0173	0	0.0174	0.0174
1	0.0104	0.0093	2	0.0097	0.0095
2	0.0059	0.0065	4	0.0067	0.0064
3	0.0045	0.0046	6	0.0050	0.0051
4	0.0037	0.0037	8	0.0044	0.0045
8	0.0025	0.0025	12	0.0037	0.0038
$t_{\frac{1}{2}}$	72	75	--	144	144 sec.

phorus now being caught on the glass tube. Next the sheath was raised and a similar run carried out. The area upon which the deposit was now

of phosphorus remaining stationary. Upon increasing the temperature of the filament, deposition recommenced. To find whether the stream density did actually attain a critical value for phosphorus to be deposited, R.V. II. was employed in the following manner. By means of the windlass, the glass tube was lowered so as to surround both filaments and a clean up run made, the red phos-

being formed was 1390 cm.^2 compared with 15.7 cm.^2 or a 10^2 -fold increase. Four typical runs are quoted in Table II and it will be seen that the half life of the P_4 molecules is not affected at all. It may be added that, after a number of runs had been carried out without the sheath, the surface of the large bulb was uniformly covered with red phosphorus. These experiments show conclusively that the stream density has nothing whatever to do with the probability of deposition and that the rate of "polymerisation" is likewise independent of the number of molecules striking the surface per cm.^2 per sec.

Calculation of the Theoretical Half Life. As was stated above, R.V. II. was so dimensioned that if all the molecules striking the filament reacted, the half life would be conveniently measurable. From the Herz-Knudsen effusion equation the rate at which P_4 molecules at 15° and at a pressure of 1 mm. strike the filament is 1.85×10^{20} per sec. per cm.^{20} k the unimolecular velocity constant is defined by $k = (-dp/p) dt$. If A is the effective area* in cm.^2 , n the number of molecules striking the filament per cm.^2 per sec. at 1 mm., V the volume of the reaction system in c.c. and N the number of molecules per c.c. at 1 mm. pressure at 15°C. , then

$$(-dp/p) dt = \frac{nA}{V \cdot N} \cdot k.$$

$$\text{But} \quad t_{\frac{1}{2}} = \ln 2 / k = \frac{N \cdot V}{n \cdot A} \ln 2,$$

which is 46 sec. for R.V. II.

The half life of phosphorus vapour in R.V. II. was then determined for a number of temperatures, and in the following Table III. the results

TABLE III.

	$t_{\frac{1}{2}}$ min.	Temp. $^\circ \text{C.}$	Efficiency ϵ .
R.V. II.	13.5	965	5.7×10^{-2}
	9.7	1180	1.14×10^{-1}
	2.8	1450	2.74×10^{-1}
	2.3	1550	3.33×10^{-1}
	2.0	1640	3.83×10^{-1}
R.V. I	2.6	645	5.0×10^{-4}
	8.2	668	1.59×10^{-3}
	14.4	582	6.1×10^{-3}
	22.4	568	5.8×10^{-3}
	64.6	530	1.38×10^{-2}

of a typical series of experiments are collected. For comparison a series obtained with R.V. I. are also included. When these are graphed by plotting $\log_{10} \epsilon$ against $1/T$, it will be seen (Fig. 4) that at low efficiencies the line is nearly straight, the slope corresponding to an apparent energy of activation of 41 kg. cal., whereas as the efficiency rises the line curves round until it asymptotically approaches the value $\log_{10} \epsilon = 0$. The transition is gradual and shows no sign of any discontinuity. Since it is known that a clean tungsten surface may be obtained by heating to temperatures in the neighbourhood of 2000° , it is likely that at the lower temperatures employed, the molecules adsorbed on the surface are only those of phosphorus.

The fact that the observed and calculated half life periods agree so well in absolute magnitude leads to two important conclusions. The first is that all molecules which react on the filament condense as red phosphorus on the walls of the reaction vessel. Had, for example, an

* For the purposes of calculation A is taken to be the geometrical area. Cf. J. A. Becker, *Reviews of Modern Physics*, 1935, 7, 103.

appreciable fraction reformed P_4 molecules, the observed half life would not have approached the calculated value, but would have been much higher. On the other hand, if the evaporation of one active molecule had induced the reaction of several P_4 molecules to yield a polymer by the successive addition of P_4 units in the gas, the half life would have been smaller than theory predicts. This statement is also supported by the observation that surrounding the filament assembly with a sheath does not affect the reaction velocity, which might happen if a chain polymerisation had occurred with the eventual termination of the chains on the walls. It is a very remote possibility that the agreement is fortuitous, the two factors mentioned above exactly cancelling each other. What is also established from these observations is that the molecule, which ultimately forms red phosphorus, is not merely a P_4 molecule which has come into thermal equilibrium with the surface of the filament and owes its activity to this alone. Otherwise the rate of deposition

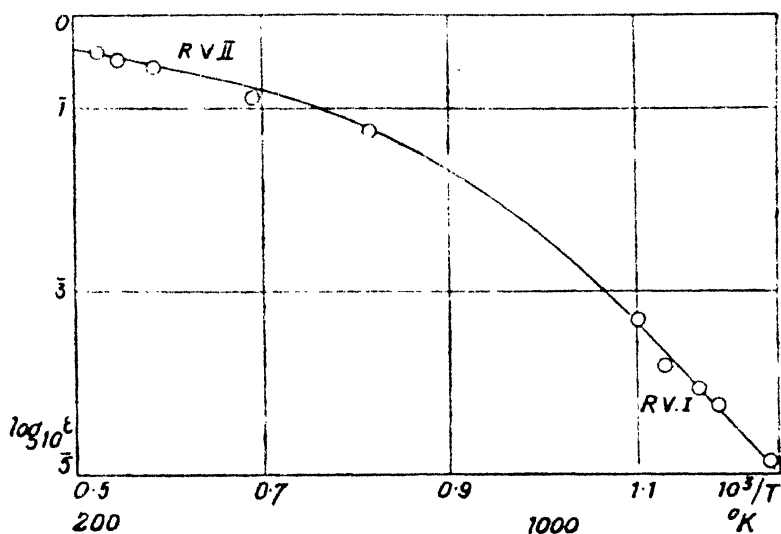


FIG. 4.

would have increased on bringing a surface closer to the filament, for then there is less chance of the energy being dissipated by collisions with other molecules on diffusing to the walls.

Energy Input to the Filament.

Since a considerable fraction of the molecules colliding with the filament at high temperature reacts, it became possible to measure approximately the energy required to activate a P_4 molecule. During each run with R.V. II, the amperes flowing in the filament were observed and also the amperes required to maintain the filament at reaction temperature in vacuo. A typical run is recorded below (Table IV.).

The excess amperes are comparatively small, but the square of the excess is approximately proportional to the pressure of the phosphorus vapour, as is shown by the last column of Table IV. The total energy E supplied to the central part of the long filament in excess of that *in vacuo* and removed therefore by the P_4 molecules is given by

$$E = R \int_0^{\infty} i^2 e^{-kt} dt.$$

TABLE IV.—R.V. II. FILAMENT TEMP. 1640.

Time (min.).	P_4	Time (min.).	Amps.	Excess Amps. over that in Vacuo (i).	P_4 Interpolated.	α .	P_4/i .
0	0.0154	0	0.379*	0.027*	0.0154	7.3×10^{-4}	21
1	0.0090	0.5	0.374	0.022	0.0112	4.8×10^{-4}	23
2	0.0061	1.0	0.370	0.018	0.0089	3.2×10^{-4}	28
3	0.0043	2.5	0.368	0.016	0.0054	2.6×10^{-4}	21
4	0.0031	3.5	0.367	0.015	0.0037	2.3×10^{-4}	16
5	0.0026	5	0.363	0.011	0.0026	1.2×10^{-4}	22
7	0.0020	7	0.362	0.010	0.0020	1.0×10^{-4}	20

Resistance of central portion of long filament 3.99ω (R).

Half life due to the above 2.0 min.

* Extrapolated.

(R is the resistance of the central part of the long filament.) But k the unimolecular constant is $\ln 2/t_1$, so integrating and substituting for k

$$E = R i_0^2 \cdot t_1 \ln 2$$

where t_1 is the half life due to the central portion of the long filament only, and i_0 is the extrapolated value of the current at $t = 0$. This amounts to 1.22×10^{-1} cal. The number of moles deposited, that is, 5400 cc. of P_4 at 0.015 mm. is 7.9×10^{-6} . The fraction of molecules reacting is 0.38. If the greater part of the energy supplied to the filament is employed in dissociating the P_4 molecules, the energy of dissociation is $1.21/4.8 \times 10^{-3}$ or 25.1 kg.cal per mole, which is in reasonable agreement with the value calculated from the variation of equilibrium constant with temperature. Two corrections, the magnitude of which it is difficult to estimate, must however be taken into consideration.

The temperature of the P_4 molecule colliding with the filament is about 15°C ., whereas the temperature of the two P_2 molecules leaving it is probably that of the filament. Secondly, the fraction (0.62) of the molecules which is not dissociated probably comes into thermal equilibrium with the filament thereby absorbing energy. The maximum amount removed in this way may be calculated as follows: The constant k of the equation relating voltage across the Pirani bridge with pressure is proportional to the accommodation coefficient of the gas on the filament and to the specific heat of the molecule at constant volume. Since no special precautions were taken to ensure a really clean surface of the Pirani gauge wire it is probable that the accommodation coefficients for oxygen and for phosphorus are nearly equal. In this case the ratio of the values of k then gives the ratio of the specific heats; that of O_2 is 5.0 cal. per mole and therefore P_4 is 7.4 cal./mole. The energy conducted away from the filament thus may become comparable with the heat of dissociation itself. The calculation of the dissociation energy is consequently subject to some uncertainty, but the figure obtained brings further support to the hypothesis that P_4 molecules are activated by experiencing dissociation.

One possible mechanism of the dissociation can, however, at once be ruled out as a result of these experiments. If it were just a question of the P_4 molecules being brought into thermal equilibrium with the surface, the "hot" molecules dissociating after leaving the filament, the fraction of molecules dissociated would be $e^{-E/RT}$ where E is, at least, the energy of

dissociation of the P_4 molecule and T is the absolute temperature of the filament. At 1600° this fraction is about 3×10^{-4} if E is 30.0 and 3×10^{-5} if E is 50.0 , compared with the observed value of 0.38 . The calculated fraction might be increased by supposing that more than two square terms contribute to the energy of activation, but the poisoning of the activity of the filament by oxygen, in addition to the evidence cited on page 276 indicates that the dissociation is a specific reaction rather than a mere heating of the molecules by transitory contact with the surface of the filament. The experiments with oxygen will be described elsewhere.

The Evaporation of Red Phosphorus. If P_2 molecules always condense to red phosphorus, and that indeed is supported by all the evidence so far available, then when red phosphorus is heated it should give off only P_2 molecules, provided the conditions are such that these may not combine to P_4 before being detected. The evaporation must therefore be carried out *in vacuo* and at low evaporation rates.

A preliminary qualitative experiment to determine whether red phosphorus may be evaporated and again condensed as the red modification was made in the following way employing R.V. III. Phosphorus vapour was admitted and deposited as the red modification on the inner walls of the furnace by heating the filament. After thorough evacuation, the furnace temperature was raised to about 400° , the reaction bulb now being placed in a bath of CO_2 and ether at -80° . The temperature opposite the furnace was a little higher, namely, -50° . The pumps were kept on during the evaporation of the phosphorus. Upon withdrawing the CO_2 bath, the pressure on the vessel rose to about 0.02 mm. and when oxygen was admitted the characteristic glow of phosphorus was emitted. In another experiment the gas evolved could be redeposited as red phosphorus. During these experiments, however, red phosphorus was also deposited at the foot of the reaction vessel, on the coolest part. With this type of apparatus it is thus evident that both P_4 and P_2 molecules are obtained on heating red phosphorus. This does not mean that P_4 molecules evaporate from red phosphorus, for the experimental conditions were such that it would not be impossible for the P_2 molecules to recombine as will be seen from the following experiments made with R.V. I and R.V. V. On carrying out similar experiments with R.V. IV, in which the red phosphorus is slowly evaporated very nearly as a collision free stream of molecules directly on to a liquid air cooled glass surface, red phosphorus only is deposited.

Effect of Reaction Bulb Temperature on the Rate of Deposition.

In the introduction it was pointed out that if the energy of a molecule in the gas phase aids its facility of reaction on a surface, there ought to be an increase in the velocity of reaction if the temperature of the containing vessel be raised. As the figures in Table V. demonstrate the phosphorus clean up exhibits just the opposite effect—the rate of reaction decreases. This at once precludes a test of the hypothesis, which however seems improbable from what was mentioned above in connection with the absolute rate of reaction and the temperature of the catalyst.

The increase in reaction bulb temperature introduces a complication unconnected with the mechanism of the reaction. The number of molecules colliding with the filament decreases in the ratio $(T_P/T_R)^{1/2}$ where T_P and T_R is the temperature of the Pirani gauge and of the reaction vessel respectively. Since the pressure in the Pirani gauge is kept constant, the pressure in the reaction bulb will increase in the ratio $(T_R/T_P)^{1/2}$, for the mean free path is comparable with the diameter of the connecting tubes. These effects thus cancel. The total number of molecules in the system will have decreased by a factor $(T_P/T_R)^{1/2}$. If V_1 be

the volume of the reaction system heated by the furnace and V_2 that of connections and Pirani the number is reduced in the ratio $(V_1 + V_2) \cdot \left(V_1 \sqrt{\frac{373}{288}} + V_2 \right)$ for the reaction vessel at 100°C . As V_1 is comparable with V_2 the correction only amounts to 5 per cent. and is neglected.

The following points, emerging from the results in Table V. are noteworthy. Although t_1 increases with temperature, when the filament temperature is kept constant the value obtained with the reaction vessel at 13.6° can also be regained by heating the filament to a higher temperature. The phenomenon is reproducible, for in the last experiment at 13.9° the original low value of t_1 is reached. These experiments could be repeated with a bulb carrying a heavy deposit or with a newly cleaned bulb. The red phosphorus deposited on the walls at low temperatures was not appreciably removed during a series of experiments involving heating the walls to 200° . On the other hand, if a clean tube were used to begin with, a visible deposit was not obtained opposite the filament as happens at room temperature when a similar amount of red phosphorus is deposited.

TABLE V.—R.V. I.

Temp. of Filament.	Initial Pressure mm.	t_1 min.	Temp. of R.V. $^\circ\text{C}$.
635	0.0104	3.8	48.5
635	0.0108	4.7	90.0
635	0.0204	0.0	148
635	0.0206	c. 20.0	161
660	0.0159	1.1	188
635	0.0174	1.0	13.6
582	0.0105	3.7	13.7
582	0.0202	10.0	59.0
582	0.0207	—	112
635	0.0107	7.2	110
635	0.0172	1.0	13.9

TABLE VI.—R.V. V.

Initial Pressure mm.	t_1 min.	Temp. of R.V. $^\circ\text{C}$.	Position of Top of Furnace.
0.0270	0.4	14.8	—
0.0150	1.5	15.4	—
0.0096	1.3	15.4	—
0.0108	2.3	83	1
0.0112	3.6	81	2
0.0124	1.5	14.5	—
0.0135	1.0	11.5	—
0.0126	2.6	85.6	1
0.0129	3.6	85.7	2
0.0100	1.6	12	—

To obtain further information about the distribution of the deposit as well as the variation of t_1 with temperature, a reaction tube similar to R.V. I. was fitted with a short filament near the bottom (R.V. V.). With this arrangement it was possible to study the distribution of the deposit as a function of the temperature of the reaction bulb.

The experiments with R.V. I. have shown that the absence of deposit opposite the filament when the reaction vessel is heated up is not due to the re-evaporation of red phosphorus to a cooler part of the reaction system, for if red phosphorus is deposited at room temperature and the tube heated to a higher temperature, there is no appreciable alteration in the distribution of the deposit. Presumably the P_2 molecules may be reflected from a hot surface but, to explain the simultaneous increase in t_1 , the P_2 's must partly recombine to form P_4 's, so that the gross efficiency of collisions with the filament is decreased. The probability of recombination also increases with rising temperature.

A further question arises with regard to the nature of the condensation. If the rate of deposition as red phosphorus is $k_1[\text{P}_2]$ and that of recombination $k_2[\text{P}_2]$, both coefficients being temperature dependent in

opposite directions, than the ratio of the probability of depositing to combining is independent of $[P_2]$ and also independent of the number of collisions the P_2 molecule makes with the surface. If therefore a P_2 molecule has to traverse a longer hot zone, repeatedly colliding with the walls of the tube, the value of t_4 should be unchanged. This condition was simply obtained by moving the furnace further along R.V.V. from position 1 to position 2. The results are given in Table VI, while the distribution of the deposit after each set of experiments is indicated in Fig. 5. The temperature of the filament was maintained at a constant value throughout these experiments.

The results with R.V. I. are confirmed by those with R.V. V. in so far as the increase in t_4 is concerned, and from Fig 5 it will be seen that

the red phosphorus is now deposited above the level of the furnace while the original deposit remains *in situ*. On raising the furnace to position 2, however, the value of t_4 still further increases and now a third deposit is formed above the furnace. This means that the greater the distance the P_2 molecules have to traverse the greater is the probability of their recombining

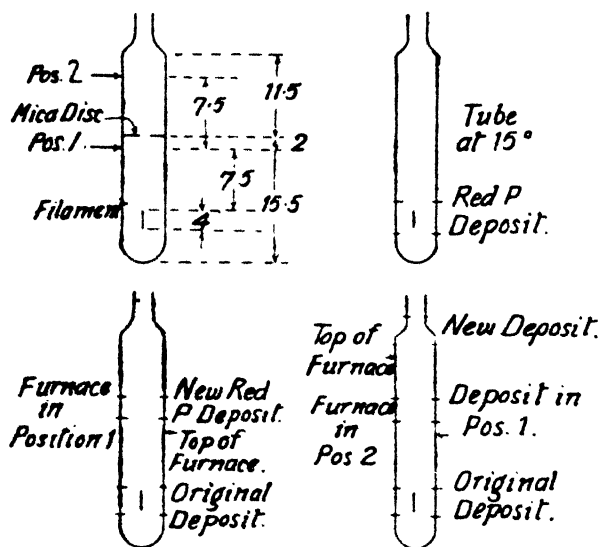


FIG. 5.

It is conceivable that the P_2 molecules migrate along the surface of the glass to the cool part of the tube. To find whether this is the case, a mica disc was suspended about the middle of R.V. V. with a rectangular opening 4×7 mm. in order to let the filament leads through. The edge of the disc only just touched the walls of the reaction vessel at a few isolated places. The disc was placed above the top of the furnace in position 1 so that if gas diffusion took place the disc would intercept the P_2 molecules on their way to the cool surface. Upon examining the disc after carrying

out an experiment it was found to be covered with a uniform red deposit which obviously had not migrated from the points of contacts of the disc with the walls. The conclusion is, therefore, that the P_2 molecules diffuse through the gas, being reflected at the walls of the reaction tube.

Owing to its position the disc was at some temperature between 15°

TABLE VII.—MICA DISC IN R.V. V.

Initial Pressure mm.	t_4 min.	Temp. of R.V.	Position of Furnace.
0.0102	1.8	13.9	—
0.0183	5.0	79	1
0.0191	7.5	79	2
0.0178	2.1	14.4	—

and 80° . A fraction of the impinging molecules would combine; the remainder would be deposited. The interposition of the disc ought to increase t_1 not only in position 1 but also in position 2, since the P_4 molecules now escape through the rectangular aperture (0.28 cm.^2) which is small compared with the cross-sectional area (3.1 cm.^2) of the reaction tube. The results in Table VII. are in accordance with expectation, the increase in position 1 and 2 being relatively much greater when the disc is interposed than when it is absent.

These results are to be compared with those in Table VI. The disc naturally does not affect t_1 when the reaction bulb is at room temperature. A decision now has to be made about the mode of recombination of P_2 molecules. If they combine in the gas, it is unlikely that a three body collision is necessary for this purpose. The time required for a P_2 molecule to reach the surface of R.V. I. is 10^{-4} sec. The rate at which P_2 molecules are produced is of the order of 10^{-4} mm./sec. , and so the stationary concentration is 10^{-8} mm. In 10^{-4} sec. one P_2 molecule would make 10^{-5} collisions with other P_2 molecules on diffusing to the walls and therefore gas phase recombination may be neglected in this vessel. Even in R.V. V. where diffusion occurs over a maximum distance of 15 cm., the probability of two P_2 's colliding is about equal to that of reaching the cool surface. It would seem, therefore, when the temperature of the walls is raised, a decreasing fraction of the molecules form red phosphorus, the remainder diffuse to the cool surface but in so doing a fraction recombine on the walls. At higher temperatures P_2 molecules must again remain unassociated, for it has been shown that P_4 molecules on passing through a hot silica jet are dissociated to P_2 . Moreover this is a necessary consequence of the theory that P_2 molecules are in equilibrium with red phosphorus and therefore condense as such on colliding with red phosphorus.

Conclusion.

All the evidence presented in the preceding pages points to the conclusion that P_2 molecules condense to red phosphorus and conversely red phosphorus evaporates in units of P_2 . The vapour pressure anomalies are removed if the assumption be made that P_2 molecules are in equilibrium with red phosphorus. There is therefore no more justification for regarding red phosphorus as a polymer than in supposing, for example, solid chlorine is a polymer made up of Cl_2 molecules. The structure of red phosphorus must simply be such that, energetically, P_2 molecules preferentially evaporate, whereas the white modification would appear to possess aggregates of four phosphorus atoms which are most easily detached as a whole from the solid or liquid surface. Unfortunately there are no X-ray data to give any guidance on this point.

It would therefore be more correct to term the transformation white to red phosphorus a depolymerisation reaction.

Summary.

Attention is called to certain discrepancies regarding the vapour pressures of white and of red phosphorus if, as is usually supposed, P_4 molecules are considered to be in equilibrium with both modifications. The discrepancy can be removed if the assumption is made that P_2 molecules are in true equilibrium with red phosphorus.

Experimental evidence is adduced in support of this hypothesis. First it is shown that P_4 molecules, on being dissociated to P_2 , by passing through a hot silica jet, condense to red phosphorus on striking a glass surface.

P_4 molecules may also be dissociated on a tungsten surface. The kinetics of this reaction have been studied in some detail with these results. The reaction is unimolecular and possesses an energy of activation of 41 kg.cal. at low filament collision efficiencies. By using a large bulb and a small filament it is shown that every P_4 molecule dissociated forms red phosphorus, the probability of deposition being independent of stream density over a 200-fold range. It is further shown that P_2 molecules are reflected from glass surfaces at temperatures greater than 15° C. and tend to diffuse to a cool surface if this is possible. In the temperature range 15–200°, P_2 molecules may be made to combine on a glass surface.

Red phosphorus can be sublimed to red phosphorus only, if sublimation is carried out under proper conditions.

These observations are discussed in relation to the theory that red phosphorus is a polymer of white phosphorus. It is concluded that in reality it would be more accurate to consider red phosphorus as a depolymer.

The authors wish to thank Prof. E. K. Rideal and Dr. E. B. Ludlam for their advice and encouragement during this work. One of them (H. W. M.) is indebted to the Royal Commissioners for the Exhibition of 1851 for a Senior Studentship. The other thanks the Trustees of the Moray Fund of the University of Edinburgh for a grant.

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GENERAL DISCUSSION.

Dr. R. G. W. Norrish (*Cambridge*) said: It seems to me that the authors go too far in their contention that red phosphorus is not a polymer in the true sense of the word. They state at the end of their paper that there is "no more justification for regarding red phosphorus as a polymer than in supposing, for example, solid chlorine is a polymer made up of Cl_2 molecules." This surely cannot be admitted; the liquefaction and solidification of a volatile substance like chlorine takes place through the operation van der Waals' forces, and gives rise to a solid of low melting-point which is in no sense a polymer.

The condensation of P_2 to red phosphorus, on the other hand, yields a solid of very high melting-point (ca 630° C.) in which primary valencies must be involved; this is essentially a true polymerisation. The correct conclusion from Melville and Gray's results would seem to be that while P_2 is the "monomer" red phosphorus is the "polymer." The pressure of P_2 gas existing in equilibrium with red phosphorus is then more properly termed a dissociation pressure, rather than a vapour pressure.

We have an exactly similar phenomenon in the dipolymerisation of polyoxy-methylenes. Our own work as described in our paper, and also the results of Spence, show that between 70° and 100° C., there is a very large pressure of monomeric formaldehyde in equilibrium with the solid. This does not mean that the solid is not a polymer, but only that the chemical reaction of polymerisation is reversible for there can be no doubt from the work of Staudinger that primary valencies are involved.

Dr. H. W. Melville (*Cambridge*) said, in reply to a question by Professor Travers: That hydrogen and acetylene are primary products of the dissociation of ethylene has been shown by chemical analysis of the gas (see references in the introduction to the paper) in addition to the evidence from pressure measurements alone.

In reply to Dr. Norrish: While admitting that the analogy between chlorine and phosphorus is not perhaps the best that could be given, yet in the stricter sense red phosphorus could not be termed a polymer. As is evident from the present discussion, the definition of a polymer is, however, a very wide one, and therefore taking into consideration Dr. Norrish's demonstration of the reversible depolymerisation of acetaldehyde and formaldehyde, it would not be incorrect to call red phosphorus a polymer. But the structure based on X-ray analysis¹⁵ does not show any evidence of the existence of aggregates of more than four P atoms separated from each other by considerable distances, such as were previously imagined to occur in red phosphorus.

¹⁵ Hultgren, Gingrich and Warren, *J. Chem. Physics*, 1935, **3**, 351.

ON THE KINETICS OF THE POLYMERISATION OF 1:3 BUTADIENE IN THE PRESENCE OF METALLIC SODIUM.

BY A. ABKIN AND S. MEDVEDEV.

The many-sided study of polymerisation processes, as a result of which a polymolecular substance, in some cases similar to rubber, develops, offers vast theoretical and applied interest. Kinetic investigations must obviously play a rôle in this study. Apart from the fact that the settlement of the problems of the mechanism of polymerisation processes can be arrived at only on the basis of kinetic research, even a general investigation from the point of view of formal kinetics and the determination of the peculiarities of the phenomena of these singular processes may yield extremely interesting results.

Some interest in the kinetics of polymerisation processes arose following the successful development and the application of the concept of chain reactions to it.¹ Indeed many observations—sensitivity to light, influence of inhibitors, the frequently observed connection between oxidation and polymerisation, the wall effect—speak in favour of the chain mechanism. It is quite natural, however, that in this work on the initiation and development of the chain theory, the specific processes of the polymerisation reaction were not cleared up for a long time.

In polymerisation reactions, which frequently occur in the liquid phase with a gradual increase in viscosity, molecules take part which grow in size during the process reaching exceedingly large proportions. This must apparently have its reflection in general and molecular kinetics.

The aim of this work is to clear up the kinetic regularities in the polymerisation of 1:3 butadiene in the presence of metallic sodium. This reaction, in comparison with others, has the advantage that it has been investigated in detail by Ziegler² and his co-workers, who gave an extremely graphic and plausible plan of the action of sodium and the

¹ Semenoff, *Chain reactions*, U.S.S.R., 1934, 525.

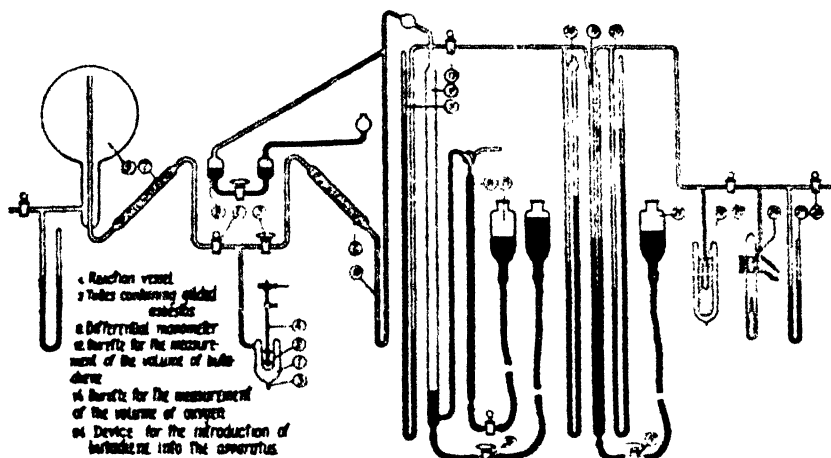
² Ziegler and Bähr, *Ber.*, 1928, **71**, 253; Ziegler, Crössman, Cleiner, and Schäfer, *Ann.*, **473**, 1; Ziegler and Cleiner, *Ann.*, **473**, 57; Ziegler, Dersch, and Wollthan, *Ann.*, 1934, **511**, 13; Ziegler, Jakob, Wollthan and Nenz, *Ann.*, 1934, **511**, 64.

other alkali metals. Moreover, a study of this reaction has also a practical interest, in view of its use in the process of the production of synthetic rubber.

In the preliminary investigations it was shown that polymerisation is extremely sensitive to oxygen, which, together with its sensitivity to light, determined the experimental conditions. The study of the polymerisation of butadiene was carried out in both the liquid and gaseous phases. Since the experimental figures and the results will be dealt with later, it is necessary in the first place briefly to note the fundamental points in the performance of the experiments and to describe the method of investigation.³

Apparatus and Methods.

The butadiene was obtained from the pure tetrabromide (m.p. = $-117^{\circ}\text{C}.$), which was recrystallised not less than five times from alcohol. The reaction took place in an apparatus which permitted the collection



Apparatus for the study of polymerization in the gaseous phase

FIG. 1.

of the butadiene in an atmosphere of nitrogen, carefully freed from oxygen. In this, butadiene was subjected to many fractionations and was collected in ampules, from which it was transferred when needed to the apparatus for the investigation of polymerisation. The latter consisted of a thick walled glass vessel (Duran) joined to a metallic valve of a special construction, which rendered the apparatus hermetically sealed under increased pressure and under vacuum. For each experiment 2 c.c. of liquid butadiene were introduced into the vessel. All the operations from the collection of butadiene to the completion of polymerisation were carried out in the complete absence of oxygen. Metallic sodium (25-40 mg.) in the form of wires 0.4 mm. in diameter was introduced in a current of pure nitrogen. Polymerisation took place in a thermostat ($+0.025^{\circ}\text{C}.$). In each experiment the amount of sodium and butadiene, the amount of polymer obtained in time t , and the quantity of unchanged butadiene were determined. Repeated experiments in which we used butadiene prepared at one and the same time were fully satisfactory, differing by no more than 3 per cent. of the weight of the initial butadiene.

³ A detailed description of the apparatus, methods, and experimental data will be published in the *Acta physicochem.*, U.S.S.R.

In the course of the work it was observed that the gaseous butadiene also polymerises in the presence of metallic sodium. For the study of this extremely singular reaction a special apparatus was constructed, shown in Fig. 1. The set-up for the gaseous polymerisation was so constructed that the process of polymerisation could be observed either volumetrically (under constant pressure) or manometrically (under constant volume). The first method has the advantage that the constant is obtained by direct measurements and therefore, for comparative measurements, it is more convenient than the manometric method.

The reaction vessel in this case was of the form of a Dewar vessel, upon the inner surface of which (on cooling with solid CO_2) a layer of metallic sodium of the desired thickness was deposited by sublimation from the ampules, which were then unsoldered. In order to duplicate results it is necessary that the entire system be completely washed with pure nitrogen and, so far as possible, completely evacuated. It was also necessary completely to remove mercury vapour and inactivated sodium by means of tubes containing gilded asbestos soldered between the reaction vessel and the whole apparatus containing mercury.

The reaction vessel is connected with a system of manometers, burettes, pressure regulators, and other devices ensuring complete and necessary accuracy of measurement. Butadiene was introduced into the system from an ampule opened electromagnetically. A burette containing oxygen was also included in the system for the study of the effect of oxygen on the polymerisation or, in special cases, for its complete poisoning.

Repetition of results on the same layer was quite satisfactory. On different layers it was not possible to obtain fully concordant results, which is quite understandable, since the rate of polymerisation depends to a great extent upon the dispersion and thickness of the sodium layer, the size of its surface, and the volume of the vessel, and on other factors the conservation of the constancy of which in different experiments is extremely difficult. For this reason all comparative measurements were made on one and the same layer of sodium.

General Description of the Rate of the Process.

In the case of technical butadiene (79 per cent. butadiene, 19.5 per cent. pseudo-butylene, and some 0.01 per cent. aldehyde) as was expected,

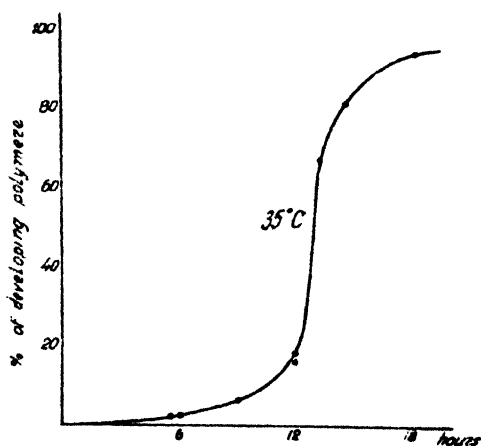


Figure 2

the experiments gave poor results. The induction period varied between 20 and 100 hours. The stages of noticeable polymerisation varied in different experiments in the same way. The absence of reproducibility was connected not so much with the presence of a large amount of pseudobutylene, which has very little noticeable effect, as with the presence of a small sometimes analytically undeterminable quantity of other substances, especially aldehyde.

Identical results were obtained only when carefully purified butadiene was used and when the experiments were performed in the absence of oxygen and light. No induction period as such was observed in this case. The process from the start occurred with increasing rapidity

and on the expiry of several periods became stationary. The form of the curve (see Fig. 2), per cent. polymerisation t , resembles the analogous curve for "branched chain" reactions ("degenerated explosions"). This resemblance is, however, only external. Actually in cases of energetic or material chains the carriers of which are comparatively unstable compounds of the type of free radicals, following the interruption of the process (*i.e.*, rapid cooling) and its subsequent renewal, results should have been obtained which do not fit into the frame of kinetic continuity. On cooling the reaction system with liquid air the results were fully identical with those received for the same period without interruption. The same is observed, but still more clearly, in the process of polymerisation in the gaseous phase and is a convincing proof of the absence of chains in the given reaction.

In connection with Ziegler's² extremely plausible assumption that the polymerisation of diene hydrocarbons in the presence of the alkali metals proceeds through metal-diene conjugate links, and in connection with the assumptions of several investigators as to the homogeneity of the process studied,⁴ we carried out experiments in the vessels shown in Fig. 3.

In vessel 1 the reaction first took place in bend *a*. After the degree of polymerisation reached a definite stage, the liquid was poured into *b* by inclining the apparatus. An extremely interesting phenomenon was then noted: polymerisation still takes place in *a*, and after some time the liquid in *b* completely disappears. The rate of this gaseous

polymerisation corresponds to the rate of the polymerisation in the liquid phase, *i.e.* under identical pressures the rates of the liquid and gaseous phase polymerisation are the same.

These experiments, however, do not exclude the possibility of a homogeneous process, since its rate, which is determined by the concentration of the sodium-butadiene compounds, must be small in comparison with that of the process occurring in the presence of sodium where, consequently, the development of new sodium-butadiene molecules continually occurs.

The absence of a homogeneous process, however, is readily shown by the experiments in vessels 2 and 3. The second vessel is bent in such a manner that, after pouring the liquid from *a* into *b*, it is possible to pour mercury contained in *c* into *a*, thus covering the sodium polymer with mercury and removing the possibility of gaseous polymerisation. The experiments in vessel 3 differed from those in vessel 2 only in the fact that, after the pouring, the bend *a* with the sodium and the polymer was

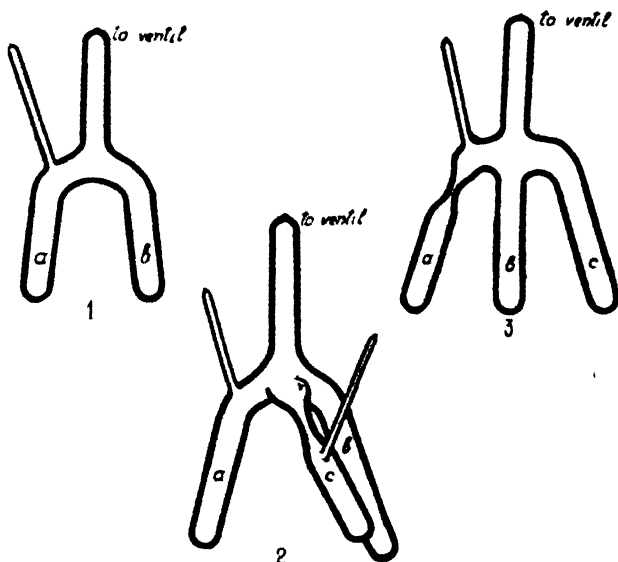


FIG. 3.

⁴ Zelmanov and Shalnikov, *J. Physic. Chem. (U.S.S.R.)*, 1933, 3, 353.

unsoldered, and thus the possibility of poisoning the homogeneous process with mercury vapour was stopped. The experiments in vessels 2 and 3 showed that the poured liquid, even after standing for many months, did not polymerise. We thus ascertained the heterogeneous character of the polymerisation of butadiene in the presence of sodium.

During the investigations of the liquid phase polymerisation, we discovered the poisonous effect of oxygen, which is easily explained by the destruction of the sodium-butadiene compounds by oxygen. This

phenomenon is, apparently, extremely typical for the polymerisation of diene hydrocarbons under the influence of the alkali metals. In other cases, especially where as a basis of polymerisation there is a clearly defined chain mechanism as, for example, during the autopolymerisation of chloroprene,⁶ oxygen is a positive factor in the rate of the process.

It has already been noted above that, under identical pressures, kinetic polymerisation is absolutely identical for both the liquid and gaseous phases.

The same peculiarities are therefore observed in the gaseous phase polymerisation, but in a more pronounced form. Furthermore, the results obtained during the study of the gaseous phase polymerisation make it possible to give a more detailed description of the kinetic process.

Just as in the case of polymerisation in the liquid phase, an interruption of the gaseous phase reaction (in this case it is more convenient not to cool but to pump butadiene out of the reaction vessel) does not disturb the normal course of the process.

Fig. 4 shows a typical polymerisation curve on a thin layer of sodium under

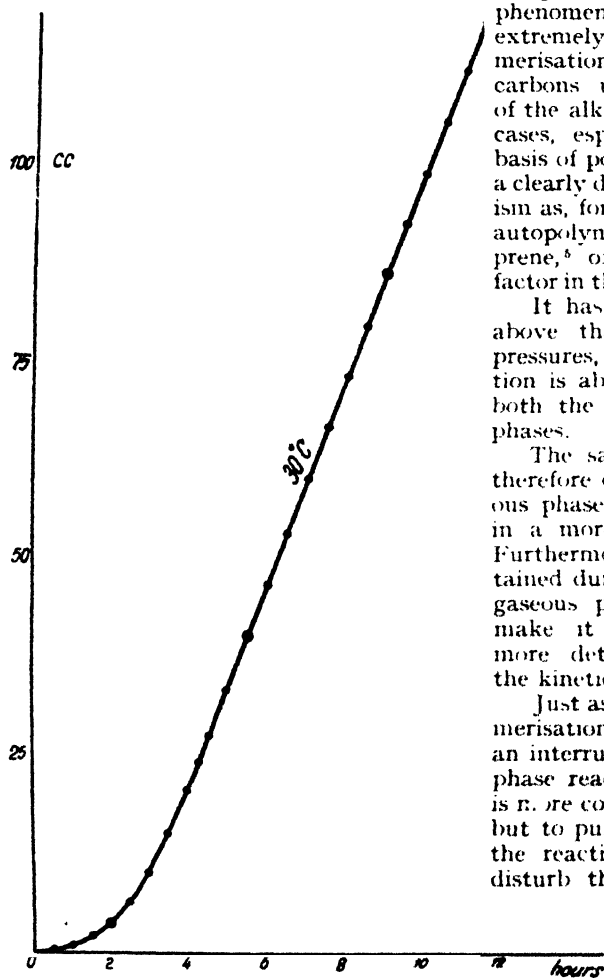


Figure 4 Polymerization in the gaseous phase

constant pressure ($p = 742$ mm.), and at 30° C. At the marked points butadiene was pumped out and then re-introduced into the system. It is noteworthy that after evacuation the previous rate is resumed only after some time since, after the introduction of butadiene into the evacuated vessel, there is always an increase in the rate due to the solution of the monomer in the polymer (in Fig. 4 this time is excluded). We see here also

⁶ This was noted by Williams and Walker, *Ind. and Eng. Chem.*, 1933, **25**, 199. (The effect of oxygen on the polymerisation of chloroprene is being studied in detail in our laboratory.)

the entire initial non-stationary period, consisting in a gradual development of the primary sodium-butadiene compounds, while all the sodium in the layer has not completely reacted.

Fig. 5 records one of the experiments illustrating the effect of oxygen. Curve 1 shows the rate of reaction prior to, and curve 2 after the addition of oxygen. These experiments were performed with a thick layer of the polymer and therefore the superimposed effects of solution are extremely large. Upon a considerable period of contact between the oxygen and the sodium-butadiene polymer, polymerisation ceases entirely. An actual difference is noted between polymerisation upon a thick and a thin layer of sodium. The difference consists in the fact that with a thick layer of catalyst in the system, there is always present metallic sodium to which the butadiene diffuses, developing new sodium-butadiene centres. This factor increases the rate

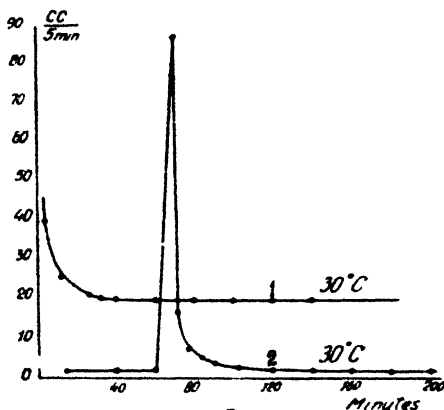
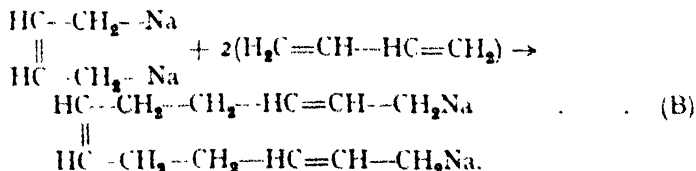
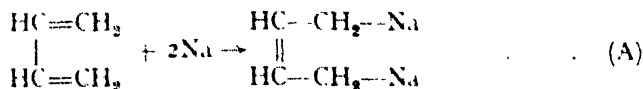


Figure 5

On the other hand the increase of thickness of the layer of the polymer serves as a gradually growing obstacle to the passage of butadiene to the sodium. Moreover, with thick layers, upon a rapid pumping out of the system the polymer peels off and a new surface of sodium is formed causing an increase in the rate. As a result of this, less clear-cut results are obtained. Systematic experiments with polymerisation in the gaseous phase were, therefore, carried out upon thin layers of sodium. In these cases, after several periods of increase in rate, a completely stationary reaction begins.

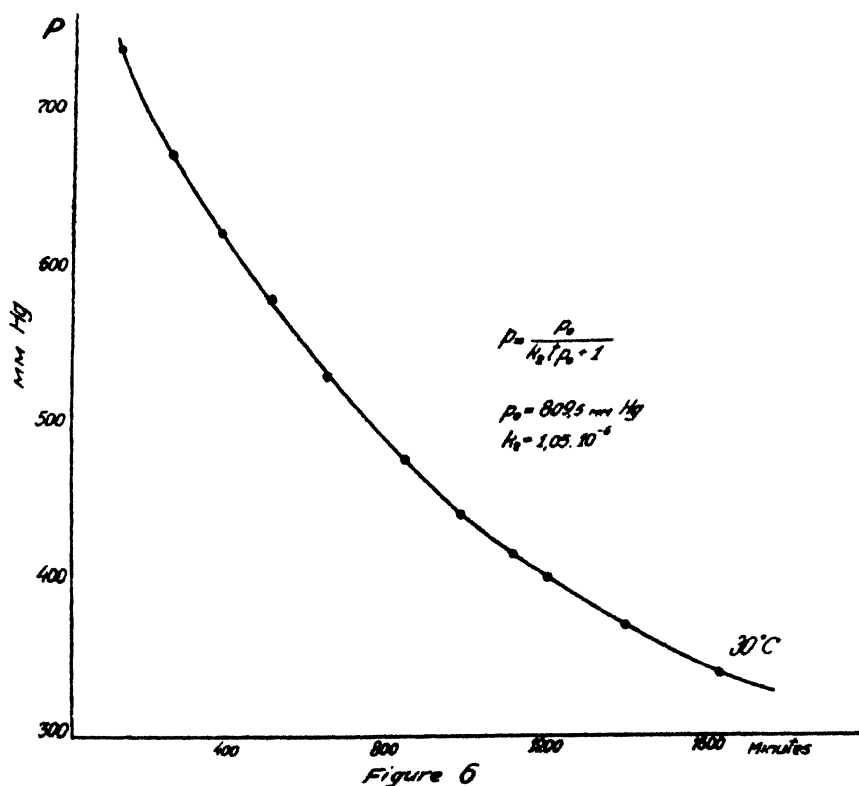
The Mechanism and Kinetics of Polymerisation.

Ziegler's data and our results point to the following general plan of the mechanism of the polymerisation of butadiene in the presence of sodium. Butadiene reacts with sodium developing primary bi-sodium compounds (reaction A). The reaction of polymerisation consists in the successive additions of butadiene molecules to these compounds (reaction B).



If the butadiene reacts with the sodium-organic compounds at its 1 and 4 carbon atoms, then the process of polymerisation can be conceived as a successive inclusion of butadiene molecules between the carbon and the sodium of the sodium-organic compound. Thus, sodium keeps

on shifting to the peripheral regions and is concentrated on the surface of the polymer where it reacts with the primarily adsorbed butadiene, a fact that might have explained the heterogeneous character of polymerisation. This general scheme, except for the surface nature of the process, as will be shown later, is proved by the kinetics of the process. The formal resemblance to, and the difference from chain kinetics, consists in that in this case the "active centres" are themselves products of the reaction: sodium-butadiene compounds, always capable of reacting with new molecules of butadiene. As Ziegler proposes and our experiments confirm, the rate of formation of the primary sodium-butadiene compounds is significantly less rapid than the rate of the subsequent additions of butadiene to the sodium-organic compounds. Thus the



appearance in a unit of time of a small number of primary centres aids the reaction of a large number of butadiene molecules. While, therefore, metallic sodium is present in the system, a non-stationary period is observed analogous to the phenomenon of "degenerated explosions," where the branching of the chains is accomplished as a result of a slowly occurring parallel or successive reaction. In this case such a parallel reaction, leading to the development of a new "active centre," is the reaction between butadiene and metallic sodium. The question as to whether or not the reaction takes place on the surface of, or within, the polymer was decided by a study of the kinetics of the reaction.

Experiments with the thick coating of sodium have already shown that, in the case of a thin layer of the polymer, diffusion of butadiene

to sodium occurs, resulting in an additional rate which is very large in comparison with the initial rate. It was further ascertained that the rate of the process depends very closely upon the square of the pressure. In Fig. 6 (where a pressure-time curve is recorded, calculated according to the bimolecular law, with the constant equal to 1.05×10^{-6} (mm. Hg. min.)) it is seen that the experimental points coincide very closely with the calculated curve. These facts do not well accord with the conception of the surface nature of the process.

The strict treatment of the reaction occurring within the polymer cannot at present be worked out, owing to the absence of necessary data (coefficient of diffusion, internal friction, etc.).

However, some of our data allow a general interpretation of the process of polymerisation as a reaction occurring within the polymer. A study of the phenomena of solution in the layer of the polymer, in which the sodium-organic compounds were previously broken by the action of oxygen, showed that the initial rate of solution is more than twice the rate of reaction. In this case it is possible that the concentration of butadiene in the polymer is determined by a condition of equilibrium:

$$\frac{C_{\text{gas}}}{C_{\text{polymer}}^n} = \text{Constant} \quad (1)$$

and during the process keeps at a constant, or nearly constant, level. The concentration and distribution of sodium within the polymer is another kinetic factor. We can infer from the constancy of the rate only that there is a constant number of sodium atoms. It is quite possible, however, that the butadiene molecules combined with the sodium-organic compounds both by their 1 and 4, as well as by their 1 and 2 carbon atoms. The absence of thread-like crystals in drawn-out butadiene rubber also speaks in favour of an interlaced net structure. The conception of a more or less equal distribution of sodium atoms within the polymer must, therefore, be considered as extremely likely, and, as an average value for its concentration, that obtained from analysis can be adopted. If we take into consideration that the coefficient of distribution

$$\alpha = \frac{p}{C^n},$$

then the dependence on the rate of polymerisation which we measure by a manometer is determined by the equation:

$$-\frac{dp}{dt} = \frac{K}{\alpha^{1/n}} p^{1/n} \quad (2)$$

We must not lose sight of the fact that the constant concentration of sodium also enters into the rate coefficient. For a correspondence of equation (2) with the bimolecular law upon which the reaction depends, it is necessary that $n = \frac{1}{2}$. As is seen from Table I., where our experimental results are recorded, this requirement is fulfilled extremely satisfactorily.

TABLE I.—THE DISTRIBUTION OF BUTADIENE BETWEEN THE GASEOUS PHASE AND POLYMER. $t = 30^\circ \text{C}$.

$p_{\text{mm.}}$	Amount in c.c. of Absorbed Butadiene in 1 c.c. of the Polymer.	$\frac{C_{\text{gas}}}{\sqrt{C_{\text{polymer}}}} \times 10^2$
636	17.92	3.81
375	6.80	3.05
293	4.32	3.58

The determination of the energy of activation (for the calculation of which, however, it is necessary to consider the temperature dependence of the coefficient of distribution) is of great interest. If the observed rate of the disappearance of butadiene as a result of the reaction is

$$w = Ka,$$

where a is the concentration or its proportional quantity (c.c. of butadiene in 1 c.c. of the polymer), then the dependence of the true rate of reaction on the temperature can be represented by a change of this relation :

$$K = W/a.$$

In Table II. are recorded the experimental results of these determinations, made under constant pressure ($p = 355$ mm.). E is the energy of activation determined from the calculation of the distribution.

TABLE II.

$t^{\circ}\text{C.}$	w (c.c. 15 min.)	a (c.c. of Butadiene in 1 c.c. of Polymer.)	$K = w/a$	$E_{\text{cal.}}$
30	2·6	11·2	0·2317	7400 7185
40	3·2	9·3	0·3441	
50	3·4	6·9	0·4921	

Neglecting the fact that, in the observed rates (w at 40° and 50° C.), the difference is extremely small and close to experimental error, the calculation of the value of the energy

of activation leads to a surprising coincidence. The value obtained for the energy of activation is considerably lower than that for a normal molecular reaction. It lies between those limits within which are found a value for the energy of activation between radicals. To conclude from this, however, that a reaction also occurs here with free radicals, is, of course, not permitted; but it points indirectly to the possibility of some preliminary activating processes which the butadiene undergoes upon solution in the polymer. The more so, that the idea of the relationship

$$\frac{C_{\text{gas}}}{\sqrt{C_{\text{polymer}}}} = \text{Constant}$$

consists in that butadiene in the polymer behaves osmotically as a dimer. If polymerisation occurs within the polymer, then for a characteristic rate of the process it is necessary to determine the rate constant of this reaction (K_2). Its rate is expressed by the equation

$$-\frac{d(\text{Bu})}{dt} = K_2(\text{Bu})(\text{Na}) \quad . \quad . \quad . \quad (3)$$

where (Bu) and (Na) are the concentrations of butadiene and sodium within the polymer.

For the calculation of K_2 we can use the data recorded in Fig. 6. The rate constant in this case equals $1·05 \times 10^{-6}$ mm./min., the volume of the system = 328 c.c., and the volume of the polymer = 1·14 c.c. Neglecting the amount of polymer during the experiment and consequently considering the concentration of sodium as constantly equal

to 5×10^{-3} mole/litre (from an analysis at the end of the experiment), we get

$$K_2 = 2.5 \times 10^{-2} \text{ mole/litre.}$$

On the basis of the value found for the energy of activation, *i.e.* 7300 cal., we find

$$K_2 = 4.7 \times 10^3 \times e^{-\frac{7300}{RT}}.$$

For the pre-exponential member we get an extremely small value, depending on the specificity of the media in which the reaction occurs.

Summary.

(1) The polymerisation of butadiene under the influence of metallic sodium was studied in the liquid and gaseous phases. The rate of the process was examined in the case of carefully purified butadiene in the absence of oxygen.

(2) It is shown that polymerisation in the liquid phase occurs heterogeneously. The rates of the gaseous and liquid phase processes are the same if polymerisation is in both cases performed under identical pressures.

(3) Independent of whether the polymerisation is performed in the gaseous or liquid phases a period is always noted at the beginning where the rate increases to a definite value, after reaching which it becomes constant. This non-stationary period is connected with the development of primary sodium-butadiene compounds, and lasts so long as metallic sodium remains in the system. The rate of this primary reaction bears only a small relation to the rate of the subsequent combinations of the butadiene with the sodium-organic compounds, later developing the final molecule of the polymer. In consequence, an external resemblance to chain kinetics is observed in the kinetics of the polymerisation of butadiene.

(4) The strong inhibiting (poisonous) effect of oxygen on the process of the polymerisation of butadiene under the influence of metallic sodium, is shown, which fully agrees with the conception of the rôle of the sodium-butadiene compound in the process studied.

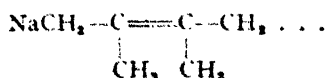
(5) The primary conception of the polymerisation as a surface process does not correspond to experimental results. An assumption is made that the process of polymerisation consists in the successive addition of butadiene molecules to sodium-organic compounds, occurring within the polymer itself. It is further shown that this assumption fully agrees with experimental results obtained in the study of the process.

(6) The rate constant of the process taking place within the polymer is determined as well as its energy of activation, together with its pre-exponential member.

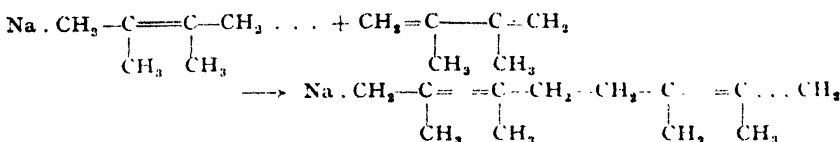
Karpev: *Institute of Physical Chemistry,
Laboratorium of Organic Catalysis,
Moscow.*

GENERAL DISCUSSION.

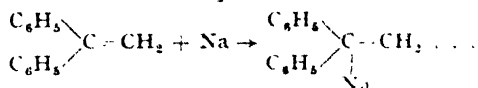
Dr. E. Bergmann (*Rehoboth*) said: Whilst during this discussion the suggestion has been stressed several times that polymerisation is a chain reaction, the mechanism proposed by the Russian authors for the dimethyl-butadiene polymerisation with metallic sodium leads to a stepwise reaction, and not to a chain. Since it is rather doubtful whether a step-reaction will account for the characteristics of a polymerisation, the following mechanism is proposed. One molecule of the diene adds *one* atom of sodium:



and gives under displacement of the double bonds a free radical. Since the latter can combine with a new diene molecule by way of a transfer of the free valency



and so on, the above radical can be a carrier of a chain. The sodium-reaction, therefore, is a real chain reaction. The suggestion made is so much the more probable, as in the laboratory of Professor Schlenk several cases have been observed where the addition of sodium metal to ethylene compounds results in the first step in the formation of a radical, *e.g.*,



which may stabilise by dimerisation or any other reaction.

The author's reply appears at the end of this number.

THE MOLECULAR WEIGHT OF POLYSTYRENES AND THE SHAPE OF THE MOLECULES IN SOLUTIONS.

BY R. SIGNER, *Bern.*

Received 7th August, 1935.

We shall give a summary of experiments on the double refraction of flow of polystyrene solutions and on their behaviour in Svedberg's-ultracentrifuge.¹ Both phenomena—the mechanically induced anisotropy of colloidal solutions, and their sedimentation in a strong centrifugal field—are dependent upon the size and shape of the colloidal particles. Our experiments are therefore likely to bring fresh material to the as yet unexhausted discussion of the structure of colloidal solutions.²

Direct Determination of Molecular Weight by the Ultracentrifuge.

Like all colloidal dispersions, the solutions of polystyrenes show the phenomenon of a sedimentation equilibrium in a centrifugal field. The

¹ Detailed publications as to the double-refraction of flow of the polystyrenes will be found in the *Z. physik. Chemie*, **A**, 1930, **130**, 257, and 1933, **165**, 161. The ultracentrifugation of polystyrenes has been fully described in *Helv. Chim. Acta*, 1934, **17**, 59, 335 and 726. The measurements have been carried out at the university laboratories of physical chemistry at Upsala, Sweden.

² The actual state of the problem of the size and form of polystyrene-molecules is as follows: H. Staudinger uses viscosity data obtained with dilute solutions to determine the length of the molecules and defends the assumption that they are straight rods; *cf.* his book *Die hochmolekularen organischen Verbindungen*, Berlin, 1932. The exactness of the viscosity method of determining molecular weights is doubted by other investigators. They imagine the most probable molecular form to be that of thread balls or clusters—see *e.g.*, W. Kuhn, *Kolloid Z.*, 1934, **68**, 2; further, E. Guth and H. Mark, *Monatshefte für Chemie*, 1935, **65**, 93.

distribution of the dissolved material in the equilibrium state permits the determination of the osmotic effects of the dissolved particles. Vant Hoff's relation between osmotic pressure and molecular weight leads to the calculation of an "apparent" molecular weight. General experience shows that, with solutions of long thread molecules the "apparent" and true chemical molecular weights are identical only in dilute solutions. At higher concentrations the apparent molecular weights turn out to be much smaller than the true ones.³ With increasing size of the molecules, the region of concentrations in which the determination of the molecular weights from osmotic pressure remains admissible becomes smaller and smaller.⁴

The ultra-centrifuge permits the determination of the osmotic effects at very small concentrations. Solutions, whose osmotic pressure does not exceed 0.01 mm. of mercury, already show a correct equilibrium-distribution in the centrifugal field, undisturbed by any secondary effects. The ultracentrifuge can therefore be used for investigations of much more highly diluted solutions than the ordinary osmometer. The molecular weights of very high molecular polystyrenes can be determined directly, without recourse to an unsafe extrapolation of the osmotic pressure towards infinite dilution.

Table I. contains the results of the ultra-centrifugal determination of molecular weights of three polystyrene-fractions. The first column

TABLE I. VISCOSITIES AND ULTRACENTRIFUGAL MOLECULAR WEIGHTS OF POLYSTYRENE FRACTIONS.

Relative Viscosity of Polystyrene in Chloroform (1 g. per litre)	Apparent Molecular Weight M at Concentrations c (g. per litre).		Real Chemical Molecular Weight.	Molecular Weight from Staudinger's Viscosity Rule.
	c .	M .		
1.026	1.0	30,000	30,000	15,000
1.054	0.8	80,000
..	1.0	75,000	80,000	31,000
1.230	0.4	300,000
..	0.9	270,000	300,000	135,000
..	2.7	120,000

The molecular weights of the three polystyrene fractions are to the first approximation, proportional to their specific viscosities. The measurements thus confirm, for high-polymers, a law formulated by Staudinger for low molecular substances. Hydrodynamics requires that the specific viscosity of a solution of rod-shaped molecules should increase roughly with the square of the molecular weight.⁵ If the values of the molecular weights, given in Table I.,

³ From the more recent experiments we may quote those by K. H. Meyer and R. Lühdemann, *Helv. Chimica Acta*, 1935, 18, 307.

⁴ See *Helv. Chim. Acta*, 1935, 18, 701.

⁵ The possible error is so wide because of the poly-dispersity of the fractions and the necessity of using an approximation method for the calculation of the mean molecular weights, see *Helv. Chim. Acta*, 1934, 17, 335.

⁶ See e.g., W. Kuhn, *Kolloid Z.*, 1934, 68, 2.

obtained by the ultra-centrifuge, are to be trusted, then either the molecules of the polystyrenes are far from being straight rods, or the laws of hydrodynamics are no more valid in the case of very thin threads. In the next sections we shall describe experiments which prove the unsatisfactory character of the usual hydrodynamic treatment, and make it probable that the polystyrene molecules in fact are more or less linear.

The Velocity of Sedimentation.

With centrifugal fields of the order of about 10^5 times the gravitation constant, the velocity of sedimentation of polystyrene solutions can be studied over a wide interval of concentrations. A safe extrapolation gives the sedimentation velocity for an infinitely small concentration, *i.e.*, for a state in which the molecules move freely in the solvent. These extrapolated values will be discussed first.

In column 2 of Table II. we find the values in question for the three

TABLE II.—SEDIMENTATION VELOCITIES s^* OF POLYSTYRENES.

Mean Molecular Weight.	Sedimentation Velocity $s \times 10^{13}$.			
	Experimental Obs.	Hydrodynamical Calculations.		
		Compact Spherical Molecules.	Spherical Clues, Total Volume 10 times that of the Molecule.	Ellipsoids, Length Equal to that of the Polystyrene Chains.
30,000	3.8	7.2	3.8	about 1
80,000	6.5	13.7	6.5	about 1
300,000	16.5	32.0	16.5	about 1

* s is the sedimentation velocity in unit field calculated from the formula

$$s = \frac{dx}{dt} \frac{1}{\omega^2 x}$$

denoting the velocity observed in the centrifugal field $\omega^2 x$; ω is the angular velocity of the rotor, x the distance of the molecule from the axis.

molecules to form spherical balls occupying a volume about ten times that of the polystyrene-thread itself, nine-tenths of the total volume being occupied by the solvent. If we suppose that all these molecules of the solvent are bound to the polystyrene threads by solvation forces and move with them in the liquid, we obtain the sedimentation velocities given in the fourth column, which agree well with the experimental values. The last column contains sedimentation velocities calculated for straight ellipsoidal particles of the length of the polystyrene molecules. In calculating these values we have taken into account the variation of the velocity with the relative orientation of the axis of the molecule, and the direction

polystyrene fractions discussed in the previous paragraph, dissolved in chloroform. It is possible to calculate hydrodynamically the velocity of sedimentation from the known molecular weight and density of polystyrenes, if definite assumptions are made as to the form of the molecules and their solvation state.

For spherical molecules without solvation-clusters the values given in column 3 are obtained. The experimental values are about half those calculated in this way, as seen by a comparison between the columns 2 and 3. Imagine now the polystyrene thread

of the field. Since the ellipsoids are continually changing their orientation by a kind of Brownian agitation, we have used an approximate mean value between the highest and the lowest possible velocity. The result can be expected to hold also for slightly curved molecules. Column 5 shows that the sedimentation of straight non-solvated molecules would be much slower than that found experimentally. Solvated molecules of the same kind, carrying molecules of the solvent with them, would have a still lower sedimentation velocity. The sedimentation velocity of diluted polystyrene solutions thus supports the theory that their molecules are curved threads forming some kind of compact cluster.

The results become different when more or less concentrated solutions of polystyrenes are considered. Fig. 1 gives a summary of experimental results, obtained with a polystyrene fraction (mean molecular weight

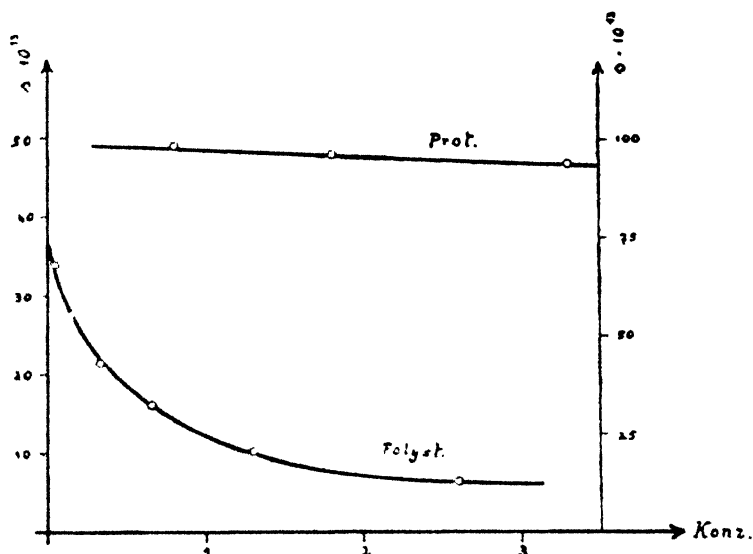


FIG. 1 -- Velocity of sedimentation of a high molecular styrene and of a protein with spherical particles, as a function of the concentration. Polystyrene dissolved in chloroform, molecular weight about 1,100,000. Protein (haemocyanin from *Helix Pomatia*) dissolved in water. Molecular weight about 6,000,000. Concentrations in grams per litre.

about 1,100,000); it represents the sedimentation-velocity as a function of concentration. For purposes of comparison, a curve showing the behaviour of spherical particles is included into the picture. The upper curve relates to an aqueous solution of haemocyanine obtained from *Helix Pomatia*.⁷ This protein has a molecular weight of 6,600,000 and a molecular radius of 125 Å. If the polystyrene clusters occupied ten times the volume of the polystyrene molecules, their radius would be something of the order of 160 Å. This spherical body would be comparable in size and shape to the protein molecule, and a solution containing such clusters as dissolved particles may be expected to show no dependence of the sedimentation velocity on concentration, in analogy with the behaviour of the protein solution. The experiments reveal, on the contrary, a great difference

⁷ See The Svedberg and E. Chirnoaga, *J. Amer. Chem. Soc.*, 1928, **50**, 1399.

between the behaviour of polystyrene solutions and that of proteins. I see no other possibility of explanation, than the assumption that the particles of dissolved polystyrene have a shape very different from that of a sphere. It seems advisable to admit at least as a working hypothesis, that the clusters of polystyrene threads are somewhat completely disentangled in solution.

The usual hydrodynamical treatment of the sedimentation of threads of this kind, at the concentrations to which Fig. 1 refers, leads also, of course, to an independence of the velocity on concentration. We may thus conclude that the usual hydrodynamical theory of viscosity does not explain the actual changes of the sedimentation velocity with concentration, and must therefore be considered as insufficient. To explain the interaction between the individual polystyrene molecules in solution, revealed by the ultracentrifuge, we must first develop a molecular kinetic theory of solutions of this kind. First, after an adequate interpretation of the sedimentation process we may hope successfully to describe the much more complicated phenomena of viscosity.

If the theory of more or less linear polystyrene threads is correct, then the polystyrene molecules must show, at low concentrations, a strong gliding against the surrounding solvent. This is the only way of explaining the high experimental values of the sedimentation velocity, as compared with those calculated theoretically for straight particles (see columns 5 and 2 in Table II.). A gliding appears not improbable, if one thinks of the small cross-sections of the threads and a certain kinetical independence of their individual sections.

On the whole, we can deduce from the sedimentation phenomena of the polystyrenes in solution, that the movement of the dissolved particles relative to the solvent is governed by laws more complicated than those so far used in the theoretical discussions of the viscosity problem. It may be suggested that the specific dependence of the sedimentation velocity on concentration is a direct proof of the long rod-shaped form of the molecules. If this were true, and the threads were not bound up into a cluster, their gliding capacity could be considered as proved.

We are now in a position to speak of the sedimentation of mixtures of two polystyrene fractions, because the phenomena observed in this case are also bound up with the thread-like structure of the molecules. Out of a mixture of spherical particles with different radii the individual particles will sediment with their own characteristic velocities, in conformity with Stokes' law: even at relatively high concentrations where will be no interaction. On this basic assumption is founded, for instance, the molecular weight analysis of protein mixtures containing components of different size.⁸ Polystyrene fractions of very different mean molecular weights, mixed in a solution, give a sedimentation curve with discrete steps only at very low concentrations. As soon as the dilution becomes somewhat smaller (but still high enough to enable spherical particles to move with complete freedom), the sedimentation diagram of a mixture of two polystyrene fractions shows only one concentration step; the lighter and the heavier particles move with the same mean velocity.⁹ This effect hardly can be explained otherwise than by a

⁸ See Thé Svedberg, *Ber.*, 1935, **67A**, 117.

⁹ Details can be found in *Helv. Chim. Acta*, 1934, **17**, 726.

mechanical entanglement of the molecules. No such entanglement would ever occur, if the single molecular threads formed compact balls; we must suppose them, on the contrary, to be more or less straight threads.

Double Refraction of Flow.

In order to obtain more detail as to the form of polystyrene molecules in solution we made a thorough investigation of the double refraction of the flowing solutions. The following conditions were varied: the gradient of flow, concentration, molecular weight of the polystyrene and the nature of the solvent. In this case again, analogous to those of viscosimetry and of ultracentrifugation, the dilutest solutions yield the clearest result. We therefore developed the usual apparatus of Couette in order to permit readings to be taken at very low concentrations.

Certain new theories form the basis of the discussion of the phenomena. The theory of P. Boeder¹⁰ is the first; this author considered the orientation of long stiff linear anisotropic particles in a flowing liquid. The degree of orientation is determined by the gradient of flow and a diffusion-constant. The latter is due to Brownian movement. The orientation of the particles determines the extinction-angle of the flowing system. The degree of orientation, the inherent anisotropy of the particles and their concentration in the solution are factors which govern the intensity of the double refraction. W. Kuhn tried to calculate the degree of orientation from the dimensions of the particles and the viscosity of the solvent.¹¹ The deductions are based on hydrodynamic formulae and doubts arise as to the possibility of using these for polystyrenes. W. Haller investigated the orientation, not only of rod-shaped molecules, but also of spherical particles, first elongated and then orientated by the flow.¹² The double refraction in this latter case depends not only on the gradient of flow and the Brownian movement, but also on a number of constants characterising the elastic and optical properties of the particles. In the following the most important experimental results will be described, and compared with the predictions of the orientation theory. Conformity with these predictions can be interpreted as a confirmation of the premises of the theory, i.e., of the linear form of the molecules. A comparison of the experimental results with the theory of elongated spherical particles is somewhat uncertain, owing to the great number of constants involved. We must bear in mind that under suitable circumstances the elongation effects may be not very different from the orientation effects, and the experiment may therefore be incapable of discriminating between them.

A. The Sign of the Double Refraction of Flow.

The double refraction of all polystyrene solutions in the usual solvents—benzene, toluene, tetraline, ethylene-bromide, bromobenzene, dioxane, etc.—is *negative* in respect to the long axis of the particle. A negative effect of this kind occurs with very few substances. It has been observed previously with poly-indene,¹³ with esters of poly-acrylic acid¹⁴ and with

¹⁰ *Z. Physik*, 1932, **75**, 258.

¹¹ Quantitative discussion of the viscosity and the double refraction of flow of suspensions can be found in *Kolloid Z.*, 1933, **62**, 269.

¹² "Orientation and deformation of disperse particles in flowing liquids," *Kolloid Z.*, 1932, **61**, 26.

¹³ *Z. physik. Chemie*, 1930, **150A**, 264.

¹⁴ *Ibid.*, 1931, **152A**, 58.

highly nitrated cellulose.¹⁵ A great number of substances with long-shaped molecules—paraffins, esters of oleic acid, caoutchouc, balata, poly-vinyl alcohol, poly-ethylene oxide, ethyl cellulose, acetyl cellulose, etc., all have a positive double refraction in solution. There exists a relation between the sign of the double refraction in solution and in the solid state. The nitro-cellulose fibre is negatively double-refractive relative to the axis of the fibre, *i.e.*, the long axis of the molecules. Isotropic films of polystyrene or esters of poly-acrylic acid become double-refractive when stretched, the double refraction being negative in respect to the direction of stress. All substances with a positive double refraction of flow show either a positive double refraction in the crystalline state (referred to the long axis of the molecule) or a positive double re-

fraction of stretched films (relative to the direction of stress). This identity of the sign of double refraction in flowing solutions and in the solid state indicates that the double refraction of flow also, is based on the orientation of anisotropic particles. Since the dissolved particles are the thread-molecules themselves, it must be possible to recognise from the sign of the double refraction of flow in what direction—that of the longest or that of shortest axis—the molecules have their highest polarisabilities (*cf.* Fig. 2).

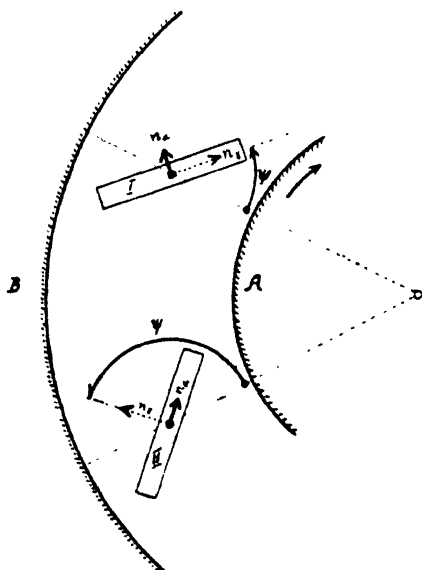


FIG. 2.—Extinction-angle ψ of rod-shaped particles with positive and negative inherent double refraction—

I. Particles with positive double refraction, $45^\circ \leq \psi \leq 90^\circ$.

II. Particles with negative double refraction, $135^\circ \leq \psi \leq 180^\circ$.

(A) Rotating cylinder. (B) Stationary cylinder.

B. Intensity of Double Refraction and the Angle of Extinction.

(a) Low Molecular Polystyrenes, with Molecular Weights from 5 to 50,000.—

All solutions show a strictly linear increase of the double refraction with the flow gradient G . This rule can be confirmed in the whole region from the

weakest currents just producing a measurable double refraction up to the beginning of turbulence. The proportionality between the optical anisotropy $(n_y - n_x)$ and the gradient G permits the characterisation of each solution by a constant $(n_y - n_x)/G$, *i.e.*, the optical anisotropy corresponding to unit flow. One and the same polystyrene fraction dissolved in a given solvent gives increasing $(n_y - n_x)/G$ -values with growing concentration. The anisotropy increases more quickly than proportional to the concentration, as shown by Fig. 3. This figure shows also the relation between molecular size and double refraction at constant concentration. If different solutions containing the same mass of

¹⁵ *Z. physik. Chemie*, 1933, 165A, 172.

polystyrene per litre are compared, one finds that $(n_y - n_x)/G$ increases roughly proportionally to the molecular weight.

It is important to be able to compare the intensity of the double refraction of flow of polystyrenes with that of some other well-defined substances. We included therefore in Fig. 3 a dotted line indicating the anisotropy of ethyl oleate in the same solvent. The double refraction of the ester is positive. The lowest molecular polystyrene contains about 100 C-atoms in the chain, oleic acid about one-fourth of this number. The double refraction of the polystyrene is approximately ten times that of the oleate. The same order of magnitude of the effects in both substances speaks rather clearly for the same cause being responsible in both cases. The assumption of an elongation of spherical balls as the cause of the double refraction of polystyrenes thus becomes

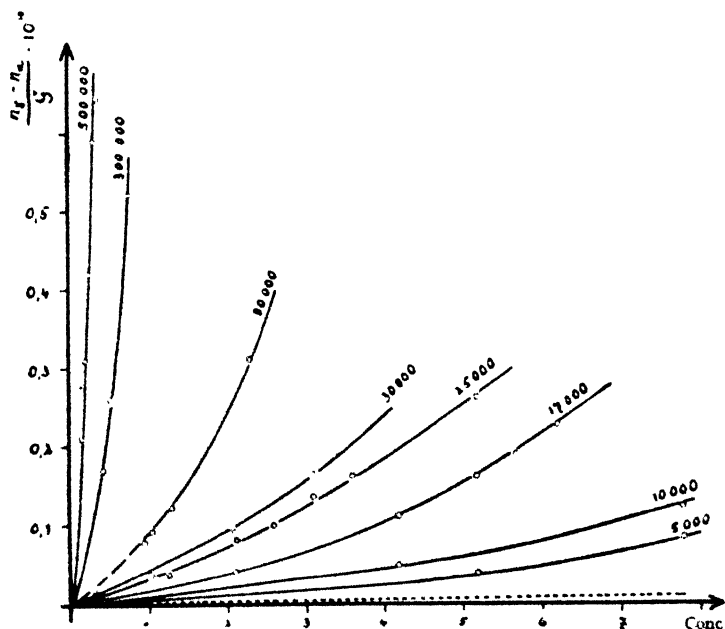


FIG. 3.—Anisotropy of different polystyrenes dissolved in cyclohexanone: (unit flow gradient). The numbers with which the single curves are inscribed are the approximate molecular weights of the fractions. The concentrations are in gm. per litre. The dotted line shows the double refraction of ethyl oleate in cyclohexanone.

less probable, since it is known that in the case of oleic acid the cause is definitely an orientation of rod-shaped molecules.

With low molecular products (molecular weight 5 to 30,000) the extinction-angle is always 135° , independent of gradient and concentration. The meaning of the extinction-angle is explained by Fig. 2. With molecular weights of the order of 50,000 deviations of the extinction-angle from the value 135° by a few degrees begin to occur, especially at high concentrations and high flow-gradients.

The constant extinction-angle 135° means, according to the orientation theory, that the desorientation by the Brownian movement is a much quicker process than the orientation by the flow. Under these circumstances the degree of orientation remains very small even at the

highest experimentally attainable flow gradients. In this region of small effects, theory predicts a proportionality between the double refraction and the flow-gradient. This is confirmed by experiment. With increasing molecular weight the Brownian movement becomes less intense and the desorientation slower. This is the reason why solutions of homologous polymeric substances of the same concentration, must show increasing double refraction with increasing molecular weight. This prediction is also confirmed by experiment. We may say that the double refraction of flow of low molecular polystyrenes completely confirms to the rules of the orientation theory.

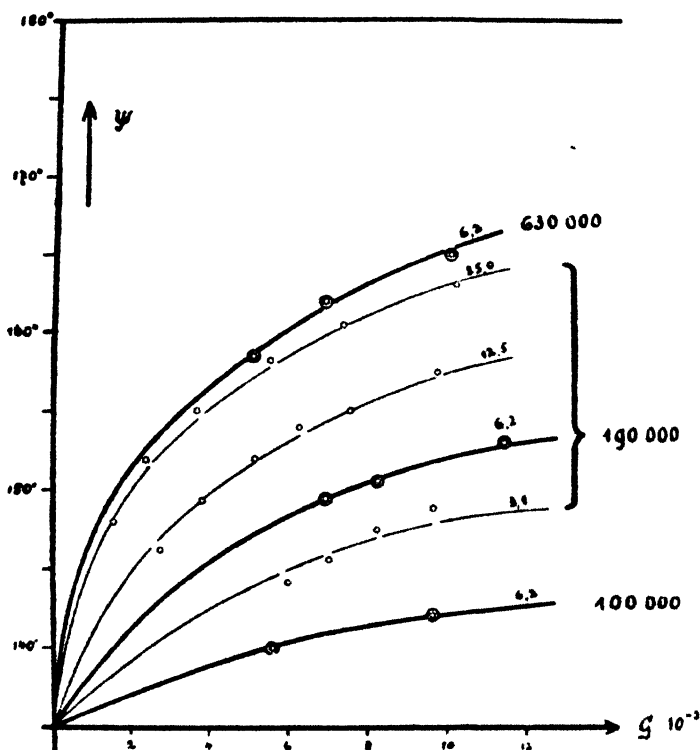


FIG. 4.—Extinction-angle ψ of different polystyrenes as a function of the flow-gradient. The numbers 100,000, 190,000 and 630,000 are the approximate molecular weights of the fractions. The numbers with which the single curves are inscribed are concentrations in gm. per litre. Solvent: bromobenzene.

(b) **High-molecular Polystyrenes with Molecular Weights from 100,000 to 1,000,000.**—With molecular weights up to 300,000, the double refraction still increases proportionally to the gradient of flow. The simple relation $(n_y - n_x)/G = \text{const.}$ still holds and the increase of the anisotropy with concentration can be represented by plotting this constant against concentration in the same way as was done in Fig. 3 for lower molecular substances. At the highest molecular weights (over 500,000) the double refraction begins to increase more quickly than proportional to the gradient of flow.

The extinction-angles are much higher than 135° . Fig. 4 shows the variation of ψ with the increasing gradient of flow for some polystyrene

solutions in bromobenzene. The thick lines correspond to equi-concentrated solutions with molecular weights equal to 100,000, 190,000 and 630,000 (6.2 g. per litre). The thin curves show ψ as a function of concentration for a substance with a molecular weight of 190,000.

We will try to compare the experimental results with the predictions of the orientation-theory in the case of high-molecular products too. The curve which represents the extinction-angle as a function of the flow gradient is, for all solutions, in qualitative agreement with theory. The relative positions of the group of curves corresponding to different molecular weights are also in agreement with theory. An increase of molecular weight means a diminished intensity of thermal agitation, and therefore a better orientation of molecules at the same concentration and the same gradient of flow. The extinction-angle must thus increase with increasing molecular weight. The observed variation of ψ with concentration of a given substance at constant flow is in agreement with theory. Rising concentration leads to a stronger interlacing and entanglement of the single molecules, and thus to a slower desorientation by thermal shocks. The extinction-angle must therefore become greater in accordance with the experimental result. Only at one point does experiment yield results disproving the theory: with solutions whose extinction angle differs appreciably from 135° , the anisotropy must be expected to increase more slowly than proportionally to the gradient of flow. The experiment shows, however, a proportionality between $(n_\delta - n_\alpha)$ and G , and at very high molecular weight even a still more rapid increase of $(n_\delta - n_\alpha)$. The orientation theory does not explain this behaviour. In the following paragraph we shall try to find a form of thread molecules which could explain all the phenomena observed.

C. Form of Polystyrene-molecules which would be in Agreement with the Phenomena of Double Refraction.

The agreement between the orientation theory and experiment at "low" molecular weights favours the assumption that the most probable form of the molecules of low molecular polystyrenes is linear. No theoretical or experimental arguments suggest, however, the assumption of rigid molecules; certain deviations from the linear form are therefore quite probable to occur. The assumption is only that an energy is necessary to bend the molecules and that they have therefore a tendency to straighten themselves out again. An explanation of this tendency will be sought later. At low molecular weights we suppose the greatest number of molecules to be present in a linear state. Their double refraction of flow is practically a purely orientation phenomenon. In going over to higher molecular products, one has to consider that with growing chain-length the form of a molecule with a given radius of curvature differs more and more from that of a straight thread. We have therefore to suppose that at high molecular weights, in addition to molecules which are more or less straight rods, there occur a great number of appreciably curved molecules of different shapes. Purely geometrical considerations explain why the contribution of the latter to the double refraction must be very small. With increasing gradient of flow the curved molecules are more and more straightened. This effect explains the rapid increase of the double refraction of high polymeric polystyrenes with the gradient, which proved to be "too quick" from the point of view of the pure orientation theory.

Very high molecular nitro-celluloses show a dependence of double-refraction on the flow gradient which is nearly in agreement with the orientation theory.¹⁶ We can consider this as an indication that the deviations from the linear form are, in this case, much smaller than in the case of the polystyrenes. Stereochemical considerations support this suggestion.

The above discussed conception of the form of polystyrene molecules in solution is based on the assumption of a tendency of molecules to straighten themselves out. To make the theory plausible, one has to find an explanation for the forces which are responsible for this tendency. We bear in mind in this connection, the resistance against free rotation around the C—C bond, which has been discovered in the ethane molecule. A resistance against rotation seems, however, not to suffice as an explanation of the straight form of long molecules in solutions. The following idea may explain to some extent the tendency of molecular thread-balls to disentangle: the individual parts of the long thread molecule have, to a certain degree, the properties of small separate kinetic units. A cluster formed by a polystyrene thread is therefore comparable to a swarm of small molecules, resembling that which exists in the first moments after the dissolution of a small crystal. Sooner or later diffusion distributes the molecules of the swarm more or less evenly throughout the whole of the solution. An analogous osmotic phenomenon will cause the molecular ball to disentangle as far as possible. The linear form appears from this point of view to be only a question of statistical probability. Deviations from the straight form are effects analogous to the fluctuations of the concentration of a solution. But a statistical treatment of this kind will surely lead to results concerning the most probable form of the molecules quite different from those obtained by the purely geometrical statistics of different possible situations, as developed recently by some authors.¹⁷

D. Double Refraction of Flow and the Abnormal Viscosity of Polystyrene-solutions.

The solutions of lower-molecular polystyrenes have a normal viscosity—i.e., their internal friction is independent of the gradient of flow. From about the molecular weight 100,000 upwards the viscosity becomes abnormal; the internal friction decreases with increasing gradient of flow. The larger the molecules, the stronger becomes this abnormal effect.¹⁸ At molecular weight 100,000 also the deviations of the extinction-angle from the value 135° become appreciable. They also increase with increasing molecular weight. The orientation theory demands that solutions with an extinction-angle equal to 135° shall have a constant viscosity. The stronger the orientation of particles in the direction of the flow (and the greater therefore the extinction angle), the smaller must be the resistances of the particles against the flow of the liquid.

This agreement between optical measurements and viscosity data from the point of view of the orientation theory forms another argument for the assumption of a more or less linear structure of the molecular threads of polystyrene. Abnormal viscosity is in this case a purely

¹⁶ *Z. physik. Chem.*, 1933, 165A, 161.

¹⁷ W. Kuhn, *Kolloid Z.*, 1934, 68, 2; further, W. Guth and H. Mark, *Monatsheshefte Chemie.*, 1935, 65, 93.

¹⁸ *Die hochmolekularen organischen Verbindungen*, Berlin, J. Springer, 1932, p. 188 ff.

orientation-phenomenon, and it must be possible to find quantitative relations between the extinction-angle and the internal friction.

E. Double Refraction of Flow in Different Solutions.

In a great number of solvents—e.g., benzene, toluene, tetraline, and bromobenzene—the relative viscosities of the polystyrenes are the same. The velocities of sedimentation in the ultracentrifuge are also identical in these different solvents (if reduced to the same differences of density and the same viscosity). Another constant property of these solutions is their light-scattering (reduced to the same difference of refractive-indices). Finally, the phenomena of double refraction of flow are very much alike in all these solutions. We may therefore assume the state of the dissolved particles to be the same.

There exist a number of solvents in which all the above-mentioned properties prove to be different. The relative viscosity of polystyrene solutions in these solvents is very low, the sedimentation-velocities very high, the light-scattering extremely strong. The double-refraction of flow appears also abnormal. The extinction-angles are extremely small. The sign of the double refraction may even be changed. The phenomena are too manifold to be explained by one single cause. We may imagine that in certain liquids the molecules are strongly interlaced, in others there may be even a formation of micelles, etc. A more detailed discussion will not be possible until other classes of substances have been investigated.

THE MAXWELL EFFECT IN COLLOIDS.

BY DR. A. M. TAYLOR.

Received 21st August, 1935.

The interpretation which is placed upon the results of measurements of streaming double refraction set up in sols has been the subject of some controversy. Signer,¹ Boeder² and others have supposed that the double refraction observed is the immediate consequence of orientation of the colloidal particles, produced by the continued shear sustained in the viscous medium in which they are suspended. The orientation is caused by the non-spherical nature of the particles, and the hydrodynamical forces involved are balanced against the thermal agitation, so that a statistical equilibrium is achieved in which there is a preferred direction of orientation of the longest axis of the particles. The particles are assumed either to be themselves optically anisotropic, or to be isotropic but of refractive index different from that of the surrounding liquid. In the first case the observed streaming double refraction is termed inherent or intrinsic, in the second it may be called "morphic" (*Formdoppelbrechung*). Kuhn³ has taken the alternative view, and supposes that the phenomenon of streaming double refraction is essentially one of photoelasticity. The particles are assumed to be isotropic in the stationary sol, but when continued shear is set up by streaming,

¹ Signer and Gross, *Z. physik. Chem.*, 1933, **165**, 161.

² Boeder, *Z. Physik*, 1932, **78**, 258.

³ Kuhn, *Z. physik. Chem.*, 1932, **161**, 427.

the Stokes forces of tension and compression to which the shear is equivalent, cause them to be deformed, so that strain birefringence is produced in each particle, the magnitude of the effect being proportional to the stress just as in the macroscopic case.

It will be appreciated without the need of quoting formulæ and figures that both theories are able to account for the facts, more especially since the chief experimental interest lies in the variation with shearing force of the magnitude of the effect and of the direction of the optic axis relative to the stream lines. There turns out to be little difference in the general description of the phenomenon whether the birefringence be ascribed to orientation of anisotropic or to deformation of isotropic particles. It is suggested that two effects associated with the names of Kerr and Ambronn may throw light on the problem.

Electric Double Refraction of Colloidal Sols.

The Kerr effect, which is the production of double refraction in an isotropic liquid under the influence of an electric field, is ascribed to the orientation of the constituent particles, be they molecules or aggregates. This orientation occurs as a result of the couple exerted by the electric field upon the dipole moment of the molecule or particle; this dipole may be permanent or induced. Just as in the Maxwell effect of streaming double refraction, statistical equilibrium is set up between the forces of orientation and thermal agitation; if the molecules are optically anisotropic, or in the case of colloidal particles even if they are only anisodimensional so long as the surrounding medium is of different refractive index, then the liquid becomes doubly refracting and the optic axis coincides with the preferred direction of orientation, *i.e.* with the electric field. Information has very naturally been sought from the Kerr effect as to the shape and properties of colloidal particles, as well as from the Maxwell effect, but the two phenomena appear to have been invoked separately and not simultaneously.

The usual method of observation of streaming double refraction is that suggested by Stokes, in which the liquid is contained in the annular space between two concentric cylinders, one of which is fixed while the other rotates, so that the stream lines are concentric with the cylinders. The optic axis everywhere coincides with the stream lines in the limiting cases of large particles or of high shearing velocity (less than that at which turbulence sets in). For low shearing velocity it may tend towards the direction of the equivalent Stokes force of tension, *i.e.* 45° to the stream lines.

If now an electric potential difference were to be applied between the two concentric cylinders the field would be radial. The double refraction resulting would be that due to the combined effect of the two fields of force, the one mechanical and the other electrical. Assuming for the moment Kuhn's view of streaming double refraction to be true, there should be no change of optical properties of the streaming liquid on switching on the electric potential. Even if the particles are electrically anisotropic, so as to be influenced by the field, they are supposed to be optically isotropic. If they are spherical orientation of their dipole moment by the field will certainly have no effect. If on the other hand the opposite view be taken that the particles are anisodimensional then they will be affected by the application of an electric field, and if they possess in addition a permanent

dipole moment the influence of the electric field will be so much the stronger. If the particles have inherent optical anisotropy, and it is their orientation which is the cause of streaming birefringence, then on switching on the electric field there should be observed a change of direction of the optic axis of the streaming liquid; the change would be such as to tend to swing the optic axis into the radial direction. The magnitude of the change would depend upon the relative strength of the electric and mechanical forces of orientation, so that from a knowledge of some of the constants of the particle others may be inferred, *e.g.* axial ratio, dipole moment, etc. Thus considerably more information may be gained as to the character of the colloidal particle by the simultaneous study of the Kerr and Maxwell effects, than of either separately; in addition the method provides a crucial experiment to decide the truth of the two rival theories of streaming double refraction.

Dichroism.

Ambronn⁴ in a series of beautiful experiments showed that colloidal materials such as cellulose and its derivatives consist of micelles arranged either at random or in parallel orientation. When dyed with suitable dyes such material becomes, in the latter case, dichroic and the optic axis coincides with the direction of orientation. Freundlich⁵ found that vanadium pentoxide sols exhibited not only streaming double refraction but also dichroism. Björnsthål⁶ examined the dichroism of lyophile and lyophobic sols, and Preston⁷ made use of the dichroism of adsorbed dye in determining the structure of both natural and artificial fibres. This type of dichroism is due to the fact that the dye molecule is itself anisotropic and therefore dichroic within the region of its own absorption band; the forces of adhesion of the dye molecule are directed and so likewise are those of the colloid micelle⁸; it follows that the orientation of the dye molecule is that of the micelles and the optic axis of dichroism of the dyed material in bulk is also the axis of birefringence of the micellar structure.

If a sol, say of cellulose acetate, is to be examined for Maxwell effect then it might also be dyed with a small quantity of "direct" dye and the streaming liquid tested for dichroism as well as for double refraction. Assuming the orientation theory of streaming double refraction, it follows that, as the adsorbed dye molecules partake of the orientation of the particles, the dichroism will always be proportional to the induced birefringence, and the optic axes will be identical. On the alternative theory of Kuhn the particles are originally isotropic, and may even be spherical as well, so that the sol only exhibits double refraction as a consequence of their photoelastic deformation. If the particles are spherical there is, on flow, no orientation, and while there may be double refraction there can be no dichroism. If the particles are isotropic but not spherical, there may be some orientation and therefore dichroism, but since the birefringence is, in Kuhn's theory, caused by deformation, the dependence of the two effects upon the velocity of shear is not likely to be the same.

⁴ Ambronn, *Ann. Physik und Chem.*, 1888, **34**, 340.

⁵ Freundlich, *Z. physik. Chem.*, 1925, **114**, 161.

⁶ Björnsthål, *Uppsala Dissertation*, 1924.

⁷ Preston, *J. Soc. Dyers Col.*, 1931, **47**, 312.

⁸ Frey, *Z. wiss. Mik.*, 1930, **47**, 1.

Conclusion.

In the electrical experiment suggested as being a crucial test of the two theories, a positive result would be evidence for the truth of the orientation hypothesis. A negative result, that is, zero change in birefringence on switching on the electric field, might merely indicate that the dipole moment of the particles remained zero. This could be checked from measurements of the dielectric constant, and of its temperature variation.

In the dichroism experiment, zero dichroism and finite birefringence, if this occurred not merely with a single dye but with many, would be strong proof of the deformation hypothesis, particularly if the behaviour of the dyes could be checked by observations with material in the gel condition. On the other hand, parallel behaviour of dichroism and birefringence would be evidence in favour of the orientation theory.

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GENERAL DISCUSSION.

Dr. R. Houwink (Eindhoven) said: Perhaps the difference between protein and polystyrene in Fig. 1 might be partly explained by assuming, in both cases, the presence of a cluster, of which the first is deformable with much more difficulty than that of polystyrene. The cause of this might perhaps be that in the protein there are present positive and negative groups, which will keep the cluster tight together, whereas such strong forces cannot be pointed to in polystyrene.

In Table I. reference is made to "real" molecular weight. Is this the molecular weight determined by the ultra-centrifuge, and is there any control which proves that this is the right molecular value indeed?

Dr. J. H. de Boer (Eindhoven) said: Following my suggestion of yesterday after the lecture of Professor Staudinger, I should like to ask Professor Signer what are the liquids in which he finds a low and a high value, respectively, for the double refraction of flow and in which a high one. Are his observations in accordance with my predictions on account of van der Waals' forces, *viz.*, that those liquids whose molecules resemble the constituents of the polymer physically give a high solvation, high viscosity, a low scattering of light and a strong double refraction of flow, whereas liquids differing much from the constituents of the polymers will give the reverse properties. In the first group of liquids one has to assume more or less stretched, strong solvated molecules, in the second group the polymers may be clustered together. I think this is in accordance with Professor Signer's views.

Dr. A. M. Taylor (St. Andrews) said: On theoretical grounds it would be of interest to examine the streaming double refraction of the same substance dispersed in a series of liquids of various refractive indices. Morphic double refraction vanishes when the refractive index of the surrounding medium equals the mean refractive index of the suspended particles, and only intrinsic and photoelastic double refraction remains. From the steepness of the curve describing, under comparable conditions of velocity gradient and viscosity, the double refraction as a function of the refractive index of the dispersing liquid, the ratio of the volume of the suspended particles to that of the liquid may be deduced.* Deviations

* Weiner, *Physik. Z.*, 1904, 5, 332.

from the theoretical behaviour would indicate that the liquids were not without influence upon the shape of the particles.

Dr. F. Eirich (Wien) said: Professor Signer and many other investigators explain the behaviour of their high molecular solutions by assuming a rodlike shape of the suspended molecules. Indeed, the elongated particle form is quite generally given as the reason for high molecular qualities. Unfortunately the practical behaviour of really rigid rods in solution is not well known. Even mathematical treatment succeeds only partially (*viz.* for the case of very strong Brownian motion), but neither this nor other approximate results are satisfactorily proved. I therefore undertook experiments with really rigid rods of well-defined axial relation. The figure (Plate I, 1) will give an idea of the rods of silk with which I worked. I am continuing the work with smaller rods exhibiting Brownian motion.

From these results one can discuss Professor Signer's experiments from another point of view. I emphasise that doubling the length of stiff rods causes a proportional increase of the specific viscosity. Further the molecules with which Professor Signer worked, which were doubtless agitated, must, if they were rigid have given rise to a greater increase in the viscosity. Of course the dependence of the sedimentation velocity on concentration indicates an elongated particle shape. But such long particles, if completely straight, would give rise to a further anomaly. There is also no reason to assume a gliding. In accordance with the hydrodynamical assumptions all these long-chain molecules with their substituents on the sides attached to liquid molecules are sufficiently large to disturb the flowing. Since even sugar molecules and hydrated ions seem to satisfy the hydrodynamical equations it follows that dimensions about ten times greater than those of the fluid molecules satisfy the hydrodynamical calculations. This argument and the fact that really rigid rods can bring about the same enormous viscosity effects as high molecular bodies enables us to explain Professor Signer's effects as due to moderately long coils into which the longer chains have become entwined.

Professor H. Mark (Wien) said: The interesting measurements of Professor Signer give an important contribution to our knowledge concerning the form of large molecules in diluted solution and I agree entirely with him that the ultracentrifuge and the investigation of the double refraction are of the greatest importance. I think also that all our present knowledge on viscosity, sedimentation, velocity, double refraction and osmotic pressure points in a certain direction concerning the shape of macromolecules in the dissolved state.

The chain-like macromolecules, which must be investigated in extremely diluted solution seem not to be compact, more or less sphere-like clusters (compare, for instance, Fig. 2a). They are, moreover, not quite extended and stiff with elastic vibrations (as shown in Fig. 2b), but they are in a state, as it is shown in Fig. 2c, that is to say, they are bent but not rolled entirely together. If one assumes the form shown in Fig. 2c one gets in fairly good agreement with all experimental evidence (Staudinger-equation, sedimentation velocity, double refraction) and remains at the same time in concordance with fundamental statistical considerations and with the principle of the free rotation round the single carbon bond. I think that the shape shown in Fig. 2c may be regarded as a close approximation to the real form of the long molecules in solution.

Professor H. Staudinger (Freiburg i Br.) said: The accurate knowledge of the shape of organic molecules is of general importance, since the physical properties of an organic substance in the solid or liquid state and in solution do not only depend on the constitution but also on the shape of the molecules.¹⁰ Take, *e.g.*, the glycol esters. If one wishes to express in the chemical formula the physical properties of the molecules,

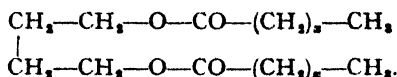
¹⁰ H. Staudinger, *Z. Elektrochemie*, 1934, 40, 434.

then the glycol esters should be written ¹¹ according to formula 1 and not formula 2 :

I.



II.



In the solid state the shape of the molecules can be elucidated by X-ray analysis which, however, in the above mentioned case has not yet been carried out. In solution the shape of the molecules can be determined by viscosity measurements, because the validity of the viscosity law $\eta_{sp}(1.4 \text{ per cent.}) = \gamma \cdot \eta$ in the case of long chain paraffins, ethers, esters, acids, both for saturated and unsaturated derivatives, proves that the thread molecules in these solutions possess a long extended shape. In these cases the viscosity of the solution, as expressed in the above formula,

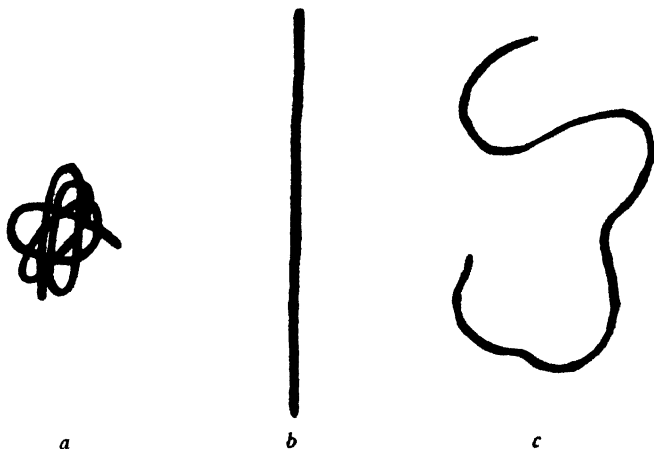


FIG. 2.

is chiefly determined by the length of the molecules and is largely independent of their diameter. When these thread-like molecules are substituted in the side chains, the viscosity of a 1.4 per cent. solution remains unchanged. Thus equally concentrated solutions of squalene and squalene hexabromide possess equal specific viscosities though the molecular weight of the latter compound is approximately twice as great as that of the former. Hence the shape of the squalene molecule is not altered by bromine substitution. The following fact shows that the thread molecules must possess a strong degree of rigidity: in the case of acetyl celluloses and nitrocelluloses the molecular weights as determined by the viscosity method and by the osmotic method agree very well with each other.¹² This idea is further strengthened by the remarkable stability of high molecular weight compounds and by the fact that even organic substances of a somewhat complicated nature crystallise readily. This could not very well be understood if the shape of the molecules in solution and in the solid state were very different. One is forced to assume that the shape

¹¹ In the above formulation tetramethylene glycol ester was chosen as example and not ordinary glycol ester, since in the latter a little complication occurs; compare H. Staudinger and H. Schwalenstöcker, *Ber.*, 1935, 68, 727.

¹² Compare this vol., p. 110.

of the molecule in the crystalline state is essentially preserved in solution, as has been proved in the cases of the paraffins, fatty acids and their esters,¹³ polyethylene oxides,¹⁴ and cellulose and their derivatives,¹⁵ for the X-ray crystal structure analysis of these substances has led to the same shape of the molecules as can be deduced from the viscosity measurements of the dissolved molecules.

Of course, thread molecules in solution cannot be compared with entirely rigid rods, but with very thin elastic rods, in which elastic oscillations about a mean position occur, these vibrations becoming larger and larger with increasing temperature. Otherwise it could not be understood why such compounds undergo intramolecular reaction with ring formation.

Mr. J. Boulton (*Braintree*) said: When cellulose is dyed with direct dyes it is believed¹⁶ that the filamentary dyestuff molecules are oriented lengthways in the direction of glucose chains and are held thus by the residual valency forces exerted by OH groups on the inner surfaces of cellulose crystallites. It is this orientation which gives rise to the dichroism which is evident in cellulose bodies dyed with direct dyes. With regard to the second part of Dr. Taylor's paper, experimental difficulties arise when we attempt to imitate these conditions in a sol. It is a simple matter to prepare a sol from esterified celluloses, but the considerations stated above with reference to direct dyed cellulose do not hold with esterified cellulose which in any case does not absorb the "dichroic" direct dyes; the present speaker is acquainted with no coloured bodies which are absorbed appreciably by cellulose acetate and which exhibit dichroic behaviour. If bodies were found which exhibited dichroism on acetate cellulose it is, further, highly likely that they would as strongly associate with any cellulose acetate solvent as with the material itself. The principal difficulty appears to be getting a cellulose sol in which the behaviour of absorbed direct dye could be studied.

Dr. A. M. Taylor said in reply: "It is regrettable that for chemical reasons the second method, that of staining the macro-molecules by oriented adsorption of a suitable dye, and observation of the dichroism induced by flow, appears to be difficult in practice. It is to be hoped that the method, which on theoretical grounds would be very fruitful, may perhaps prove useful in special cases; it is of less general application than the first method suggested of crossed electric and hydrodynamical fields. The simultaneous observation of the Kerr and Maxwell effects should be valuable in every case except the special one when the macro-molecule possesses only a negligible dipole moment."

Professor R. Signer (*Bern*), in reply: Dr. Houwink suggests that the striking decrease in the sedimentation velocity of polystyrene may be explained on the assumption that in solutions at rest, coils or clusters may be formed which are very readily deformed, and that on streaming in the capillary viscometer or in the centrifuge cell the coiled thread molecules would be more or less extended. This explanation is, from many points of view, attractive but it presents many difficulties. If polystyrene solutions are sedimented in strongly varying centrifugal fields we find a proportionality between ds/dt and ω^2x .¹⁷ If deformation occurred with increasing velocity there would be no proportionality of this kind. The sedimentation experiments which have so far been carried out provide no

¹³ Compare H. Staudinger, *Z. Elektrochemie*, 1934, 40, 434.

¹⁴ Compare E. Sauter, *Z. physikal. Chem.*, 1933, 21B, 161.

¹⁵ On the form of the cellulose molecule in the solid state, compare Sponsler and Dore, *Colloid Symposium Monograph*, 1926, 174 and further, K. H. Meyer and H. Mark, *Ber.*, 1928, 61, 593. On the shape of the cellulose molecule in solution, compare H. Staudinger, *Die hochmolekularen organischen Verbindungen, Kautschuk und Cellulose*.

¹⁶ Meyer, *Melliand*, 1928, 9, 573; 1929, 10, 31.

¹⁷ *Helv. Chim. Acta*, 1934, 17, 64, Table III.

confirmation of Dr. Houwink's interpretation. Further, the linear increase in the streaming double refraction with the velocity gradient gives evidence against an unravelling of coils. On the other hand, we do still find ourselves in harmony with experiment, if we assume that in fluids at rest the threads are fully extended.

In reply to Dr. Houwink's other question, the molecular weights in Table I. were determined by means of the ultracentrifuge; *i.e.*, from the sedimentation equilibrium. With regard to the accuracy of these values, one can only say that in very dilute solutions there are no osmotic complications.

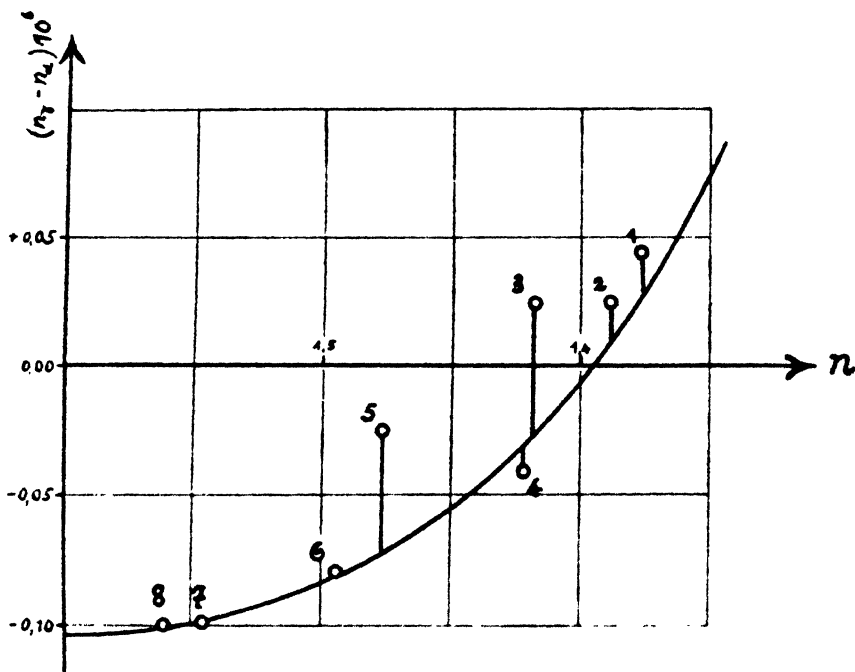


FIG. 3.—Streaming double refraction of a high polymeric styrene in solvents of different refractive index. Concentration: 13 g polystyrene per litre of solution. Streaming gradient: $G = 50 \cdot \frac{1}{\eta}$, where η is the absolute viscosity of the solvent.

- (1) Methyl ethyl ketone.
- (2) Butyl acetate.
- (3) Dioxane water mixture.
- (4) Dioxane.
- (5) Dekaline.
- (6) Toluene.
- (7) Tetraline.
- (8) Brombenzene.

The questions of J. H. de Boer and A. M. Taylor are answered by Fig. 1. It shows the dependence of the streaming double refraction of a polystyrene (mol. wt. about 100,000) on the refractive index of the solvent. The figure shows that purely rod-like morphic double refraction, without intrinsic double refraction, cannot exist. A curve can be drawn through points 1, 2, 4, 6, 7 and 8 which corresponds qualitatively to an interaction of negative intrinsic double refraction and rod-like morphic double refraction. The values for a mixture of dioxane and water as solvent and for tetraline lie off the curve (points 3 and 5). Clearly these

media have but slight solvent affinity for polystyrene. The conditions for solution are here different, as is to be inferred from other properties, such as viscosity, degree of turbidity, etc.

In reply to Mark and Eirich: The experimental conditions in polystyrene solutions can be best understood if we assume that relatively short molecules exist exclusively in the stretched form. Very large molecules will also exist in the curved form. The assumption of a tight coiling is scarcely compatible with experimental observation, at any rate in solvents with good solvent capacity. The tendency towards coiling is well understood as an osmotic effect.

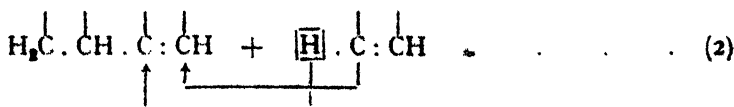
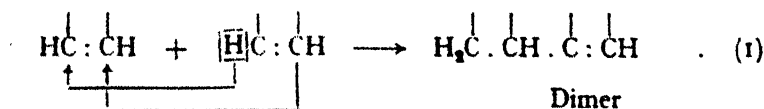
SOME OBSERVATIONS ON POLYSTYRENE AND ON THE MECHANISM OF POLYMERISATION.

By G. STAFFORD WHITBY.

Received 7th August, 1935.

Leaving aside the case of such materials as carbohydrates of high molecular weight, which cannot be regarded as polymers in the sense of substances formed by the repetition in a single molecule of a monomeric unit known to exist separately (no simple unit, $C_6H_{10}O_5$, is known from which cellulose $(C_6H_{10}O_5)_n$ is obtainable), and in the formation and behaviour of which secondary valency forces associated with the oxygen bridges may possibly play an important part, in typical cases the occurrence of polymerisation is dependent on the presence in a monomeric unit of an unsaturated centre, such as $C:O$, $C:N$ or, most frequently, $C:C$, and the repetition of such a unit in single molecules to form polymers is, according to the consensus of present-day opinion, due to primary valencies.

Studies of the polymerisation of a number of unsaturated compounds, which are capable of yielding polymers ranging up to material of high molecular weight, and including prominently compounds containing a conjugated system, especially butadienoid hydrocarbons and compounds containing a semi-benzenoid system, and, particularly, detailed studies of the polymers of indene, led the writer to the view that the union of monomeric molecules to form polymers is typically due to a succession of additions, of the ordinary, chemical type, to the double bond present in the monomer or the preceding polymeric stage, an atom of hydrogen going to one side of the double bond and the rest of the addendum to the other. For example:—



the degree of polymerisation. Brunner,⁷ working with Staudinger, measured the bromine absorption of polystyrene preparations higher than those listed in Table III., with the results in Table IV.

In these experiments, however, an absorption period of only one hour was allowed. In the experiments on which Table III. is based an absorption period of twenty-four hours was given. But even the latter period is apparently insufficient for the completion of bromine addition, to judge

TABLE II.—FRACTIONS OF
POLYINDENE (BY THERMO-
POLYMERISATION).

Expt. No.	Mol. Wt.	Atoms Br Added Per Mol.
1	553	2.00
—	583	1.96
2	506	2.99
—	669	2.11
—	778	2.11
3	414	2.00
—	574	2.07
4	519	2.19
5	474	2.08
—	892	2.28

TABLE III.

Mean Mol. Wt. of Fraction.	Average No. of Monomeric Mols. in Polymer.	Atoms Bromine Absorbed per Mol.
218	2	2.04
307	3	1.80
349	3.4	1.84
977	9	1.70
1274	12	1.46
1316 (a)	13	1.80
1979	19	1.24
2914	28	1.14
4405	42	1.26

by experiments of Staudinger and Steinhöfer⁸ published since the writer's work on polystyrene was completed. These authors found the results on Table V. for the bromine addition capacity of two samples of polystyrene (prepared by the action of stannic chloride on styrene).

It thus seems probable that, had a longer period of absorption than twenty-four hours been given in the experiments noted in Table III., the

TABLE V.—BROMINE ADDITION TO
POLYSTYRENES (STAUDINGER AND
STEINHOEFER).

TABLE IV.—BROMINE ABSORPTION
OF POLYSTYRENES (BRUNNER).

Mean Mol. Wt. of Fraction.	Average No. of Monomeric Mols. in Polymer.	Atoms Bromine Absorbed.
5,300	51	0.58
7,600	73	0.78
13,000	125	0.12

Mean Mol. Wt. (Cryo- scopically).	Atoms of Bromine Added after a Period of		
	1 day.	3 days.	4 days.
2550	1.10	1.82	2.00
3200	0.98	2.00	1.91

bromine addition of all samples would have been equivalent to two atoms per mole.

In view of the above data, it seems reasonable to suppose that polystyrenes, like polyindenes, contain one double bond per molecule, no matter what the size of the polymer.

Additional evidence for the unsaturated character of polystyrene

⁷ Brunner, *Dissertation*, Zurich, 1926.

⁸ Staudinger and Steinhöfer, *Annalen*, 1935, 517, 35.

and polyindene is to be seen in the work of Gallay,⁹ who measured the dipole moment of a series of these polymers and found it to increase with increasing molecular size—a fact explicable only on the view that a double bond persists after polymerisation.

A recent study of the polymerisation of indene made by Risi and Gauvin¹⁰ indicates that a further complication may in some cases arise from the occurrence of molecular rearrangement of the first-formed unsaturated polymer to a saturated compound (the ordinary, unsaturated diindene, for example, can be transformed, by heating, into a saturated isomer). This study does not, in the writer's opinion, invalidate the view of the mechanism of polymerisation here in question. It does, however, perhaps suggest that in studies directed to the elucidation of the mechanism of polymerisation it is wisest to choose cases where polymerisation can be brought about—by suitable catalysts or by mere standing—without the application of high temperatures. Such cases should preferably be chosen so that the products are of moderate molecular size only, since very highly polymerised materials such as spontaneously-polymerised styrene are intractable.

Addition of Monomer and Polymer.

Further evidence in support of the view enunciated as to the mechanism of the polymerisation, *viz.* that it is a succession of ordinary chemical addition reactions, is found in the fact that when a mixture of indene and diindene or of styrene and distyrene is heated higher polymers are formed. That the addition of monomer and dimer is involved in this reaction is shown by the fact that the amount of higher polymer formed is in excess of that which could have been derived from the amount of monomer which disappears.

A mixture of equal parts of styrene and distyrene heated for four days at 240° C. gave³ 76 per cent. of polystyrene, as a white amorphous solid with a mean molecular weight of 1316, equivalent to a polymerisation degree of nearly 13. A mixture of indene and diindene gave triindene when heated together.³ The lower degree of polymerisation attained in the latter case, as compared with the case of mono- and di-styrene, is in accord with the fact that in general indene does not yield such high polymers as styrene, especially when heat is used as the polymerising agency.

Experiments carried out by Houtz and Adkins¹¹ show that a higher stage in the polymerisation process can be secured by causing a lower stage and monomer to react. They showed that polystyrene of very high molecular weight and styrene are capable of adding together when heated, yielding a polystyrene of still higher molecular weight. Mixtures of styrene and polystyrene when heated together gave a yield of polymer markedly greater in amount and higher in molecular weight than was given by styrene heated alone under the same conditions.

The fact established by these various experiments that monomer and a lower polymer are capable of adding together to form a higher polymer clearly supports the view that a succession of stepwise additions is involved in the formation of long chains by polymerisation.

Further in accord with this view is the fact that it has in several cases been shown that the unsaturated molecules which represent early members in the polymerisation scheme are themselves polymerisable, albeit, as might be expected, more sluggishly than are the monomers. Diindene heated

⁹ Gallay, *Koll. Zeit.*, 1931, **57**, 1.

¹⁰ Risi and Gauvin, *Private Communication*.

¹¹ Houtz and Adkins, *J. Amer. Chem. Soc.*, 1935, **55**, 1609.

for twenty-one days at 214° C. gave 81.4 per cent. of a polyindene with a mean molecular weight of 562, corresponding to a mean degree of polymerisation of nearly 5. Treated with the polymerisation catalyst, antimony pentachloride, it gave a polymer of molecular weight 1233, corresponding to a degree of polymerisation of 10. Distyrene heated for four days at 245° C. showed indications of polymerisation, the molecular weight rising from 204 to 302. Staudinger and Steinhöfer⁸ have found that distyrene and tristyrene are polymerised by treatment with stannic chloride to the stage of a tetramer and a hexamer of styrene respectively.

Pyrolysis of Polymers.

In the case of a polymeric product, such as rubber, derived by the polymerisation of a diolefine, pyrogenic decomposition is of very limited value for the purpose of elucidating the constitution of the polymer, because of the occurrence of cyclisation in the open-chain terpenic fragments which may be supposed to represent the initial products of cracking. In the case of polymers, such as polyindene and polystyrene, derived from semi-benzenoid monomers, pyrogenic decomposition is, however, a more illuminating and less ambiguous line of investigation. When subjected to pyrolytic distillation, both polyindene and polystyrene behave in a way that accords with the conception of their constitution which has already been outlined. They undergo a typical cracking reaction, which is the converse of the reaction conceived to take place in their formation: the chain undergoes scission into fragments with the simultaneous wandering of a hydrogen atom and the appearance of a double bond for each fragment. When the temperature applied is sufficient to produce scission products which are distillable under reduced pressure, these products are—monomer, dimer, trimer, and low polymers. (When the temperature is insufficient to yield distillable products, the result of heating is to "crack" the large polymeric molecules to smaller, but still relatively large ones. Thus, *e.g.*, a sample of polyindene of mean molecular weight 2631, when heated for fifteen days at 214° C., gave no distillable products but suffered a reduction in molecular weight to 870.²)

The following Table shows the fractions obtained by the pyrolytic distillation under a pressure of 2 mm. of two fairly homogeneous samples of polyindene of different molecular weights² :—

TABLE VI.—PYROLYTIC PRODUCTS FROM TWO "HOMOGENEOUS" SAMPLES OF POLYINDENE OF MOLECULAR WEIGHTS 2631 AND 608 RESPECTIVELY.

Yield (Per Cent.)

	High Polyindene.			Low Polyindene.		
	Distillate (on Re- distillation).	Undistillable Residue.	Total.	Distillate (on Re- distillation).	Undistillable Residue.	Total.
Indene	39.5	—	39.5	13.2	—	13.2
Diindene	16.1	—	16.1	10.8	—	10.8
Triindene	22.3	—	22.3	12.0	—	12.0
Low polymers	1.6 *	8.7 †	10.3	5.1 ‡	39.8 §	44.9
Truxene, etc.	1.1	5.7	6.8	1.7	14.9	16.6
Loss	—	—	5.0	—	—	2.5
			100.0			100.00

* Mol. wt., 405.

† Was resolved into three fractions with mol. wts.—657, 531, 393.

‡ Mol. wt., 300.

§ Mol. wt., 630.

Table VII. shows the fractions obtained by the pyrolytic distillation under reduced pressure of a sample of polystyrene of very high molecular weight and one of relatively low molecular weight, obtained from styrene by spontaneous polymerisation and by heating respectively.¹²

TABLE VII.—PYROLYTIC PRODUCTS FROM A HIGH AND FROM A RELATIVELY LOW POLYMERIC PRODUCT OF STYRENE.

	I. Spontaneously Polymerised Styrene (Mol. Wt., over 56,000).		II. Heat Polymerised Styrene (Mol. Wt., 2489).	
	B.P.	Yield (Per Cent.).	B.P.	Yield (Per Cent.).
Styrene	29-31°/6-8 mm.	55.3	29°/2 mm.	42.2*
Distyrene	130-36°/4 mm.	15.1	120-22°/1-2 mm.	16.3
Tristyrene	209-16°/4 mm.	19.6	190-91°/1-2 mm.	23.7
Low polymers	—	—	208-12°/2 mm.	9.2
Undistillable residue	—	2.5	—	Nil
Loss	—	7.5	—	8.6
		100.0		100.0

* Contained a little benzene.

In the experiments both with polyindenes and polystyrenes, it was found that the more highly polymerised sample broke down more readily, *i.e.*, at a lower temperature, and more profoundly, *i.e.*, to yield a larger proportion of the smaller cracked products, than did the less highly polymerised sample. This is in accord with what happens in the cracking of simple, non-polymeric molecules. The straight-chain paraffins, for example, crack more readily, the longer the chain.¹³

Importance of Terminal Hydrogen Atoms.

The hypothesis of the mechanism of polymerisation here under discussion involves as an essential feature the wandering at each step in the process of a hydrogen atom from one molecule to the unsaturated system present in the molecule of the monomer or of an earlier polymeric stage. In accord with it is the fact that terminal substitution in the butadienoid system is unfavourable to polymerisation. Piperylene (1-methylbutadiene) polymerises less readily than isoprene (2-methylbutadiene).¹⁴ Of the dimethylbutadienes, the 2:3-compound, in which all the terminal hydrogen atoms of butadiene are unsubstituted, polymerises more readily and to a product of higher molecular weight than any of the others; the 1:4-compound, in which both terminal hydrogens of butadiene are substituted, polymerises least readily.¹⁵ The 1:1:4-trimethylbutadiene has far less capacity for polymerisation than the corresponding 1:1:3-compound. The trimethyl compounds polymerise less than corresponding dimethyl compounds. The 1:1:4:4-tetramethylbutadiene, in which all the terminal hydrogens of butadiene are substituted, is practically or entirely devoid of ability to polymerise,¹⁴ but the 1:2:3:4-compound

¹² Reference 3; *cf.* reference 8.

¹³ *Cf. The Pyrolysis of Carbon Compounds*, C. D. Hurd, New York, 1929.

¹⁴ Lebedev and Merezhkovskii, *J. Russ. Phys. Chem. Soc.*, 1914, 45, 1249.

¹⁵ Whitby and Gallay, *Can. J. Res.*, 1932, 6, 280.

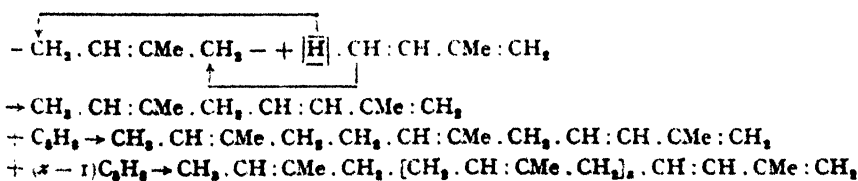
shows some capacity for polymerisation, a pentamer being isolated from it.¹⁵

A similar state of affairs holds for the phenyl-substituted butadienes: the greater the amount of substitution, especially in the terminal positions, the lower is the tendency to polymerisation.¹⁵

Carothers¹⁶ has observed similar conditions among the homologues and analogues of the highly polymerisable molecule, chloroprene (2-chlorobutadiene). Whereas alkyl substitution in the median position of the butadienoid system does not seriously affect the polymerisability of chloroprene, terminal substitution reduces it markedly, and, the larger the terminal alkyl substituent, the more seriously is the ease of polymerisation reduced. Similarly, the introduction of one or two additional chlorine atoms into chloroprene, if in the terminal positions, greatly reduces the ease of polymerisation.

Caoutchouc.

The motive behind much of the study which has in recent years been devoted to polymeric materials and to the mechanism of polymerisation has been the desire to elucidate the constitution of the important, naturally-occurring materials, rubber and cellulose. The writer has considered the question of the constitution of caoutchouc, the hydrocarbon of rubber, from the point of view of the hypothesis, outlined above, that the formation of high polymers from unsaturated compounds involves a succession of ordinary, chemical additions with wandering of hydrogen atoms.¹⁷ He has pointed out that there are three possible schemes according to which isoprene molecules might on this hypothesis undergo stepwise addition in a regular manner. Each of these leads to the formulation of caoutchouc as containing, by virtue of the presence of a terminal diolefinic system, one double bond more than the number of isoprene units involved. The following is one of the schemes in question and involves the 1:4-addition of isoprene molecules in a stepwise and regular manner:—

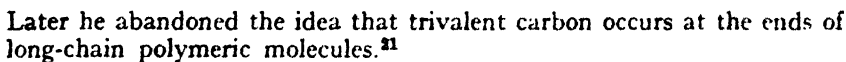


On ozonolysis such a molecule would yield α molecules of l  vulinic aldehyde or acid, and one molecule of each of the following: formaldehyde or formic acid, methylglyoxal or pyruvic acid, acetaldehyde or acetic acid, aceto-acetic acid or aldehyde. It was pointed out that, while the work of Harries had made it clear that, as would be expected if α were large in a formula such as the above, the ozonolysis products of caoutchouc are preponderantly l  vulinic aldehyde and acid, it might be expected that, if such a formula were correct, a careful re-examination of the products of the ozonolysis of caoutchouc made with a sufficiently large amount of material would disclose the occurrence in small amounts

¹⁶ Carothers and Coffmann, *J. Amer. Chem. Soc.*, 1932, 54, 4071; Berchet and Carothers, *idem.*, 1933, 55, 2004; Jacobson and Carothers, *idem.*, 1933, 55, 1624; Carothers, *Ind. Eng. Chem.*, 1934, 26, 30.

¹⁷ Whitby, *Trans. Instn. Rubber Industry*, 1929, 5, Pt. 1.

It is interesting to note that Staudinger, who has carried out extensive investigations on the subject of polymerisation, after exploring other modes of formulation for polymers, appears in some of his more recent writings to be disposed to consider that the molecules of long-chain polymers contain a terminal double bond. Staudinger originally¹⁹ held the view that free valencies existed at the ends of the molecule of long-chain polymers, but²⁰ did not make themselves evident in the possession of unsaturation by the molecule because of the large size of the latter. He supposed, for example, that caoutchouc had the formula—


$$\begin{array}{c} \dots \text{CHPh}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{C}[\overline{\text{H}}]\text{Ph}\cdot\text{CH}_2\dots + \dots \text{CHPh}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{CH}_2\dots \\ \quad \quad \quad | \qquad \qquad \qquad \uparrow \\ \rightarrow \dots \text{CHPh}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CPh}\cdot\text{CH}_2 + \text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{CH}_2\dots \end{array}$$

Of the various artificial polymers known to exhibit elastic properties, polystyrene, which was first observed by the author to show elastic properties under appropriate conditions,²³ perhaps most deserves being described, as Staudinger has described it, as a "model of caoutchouc."

²² Whitby, *Colloid Symposium Monograph*, 1926, 4, 203.

A study²³ of the colloidal and elastic properties of the two materials discloses many analogies between them. Polystyrene and rubber act similarly in regard to their behaviour to organic liquids, in regard to the nature of the liquids in which they swell and ultimately disperse, and in regard to the relative ease with which they are precipitated from their sols by, for example, the homologous series of aliphatic alcohols. Sols of polystyrene and of rubber are also similar in that the relative viscosity is not affected by change of temperature, and in that it is reduced by heating, mechanical agitation and exposure to ultra-violet light.

Although hard and inelastic at room temperature, polystyrene of high molecular weight shows at an elevated temperature (e.g., 70°), elastic properties similar to those of rubber in regard to extensibility, retractive bility, elastic after-effect, set, etc.

The most significant observation is perhaps that the colloidal and elastic properties are quantitatively influenced by the molecular weight. Polystyrene of very high molecular weight (prepared by the spontaneous polymerisation of styrene) is similar to raw rubber in the ease with which it retracts after being extended. Polystyrene of relatively low molecular weight (prepared by the heat polymerisation of styrene) shows very much poorer elastic properties; while very readily extensible, its ability to retract is poor. Thus, for example, a sample of molecular weight about 2000, when extended 800 per cent. and then released retracted to 600 per cent. only.

The solubility is also influenced by the degree of polymerisation. For example, polystyrene of very high molecular weight is unaffected by ether, acetone and ethyl oxalate, whereas polystyrene of relatively low molecular weight rapidly disperses in them.

*National Research Council,
Ottawa, Canada.*

²³ Whitby and McNally, *Unpublished Experiments*.

THE INSOLUBLE POLYSTYRENE.

BY PROFESSOR DR. H. STAUDINGER, *Director of the Chemical Laboratories,
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DR. W. HEUER AND DR. E. HUSEMANN.

Communication No. 121 in the series "*Über hochpolymere Verbindungen*."

*Received 4th July, 1935, in German and translated by
DR. I. J. RABINOVITCH.*

The following interesting observation has been made by colloid chemists: Certain lyophilic colloids, although apparently of equal composition, show a very different capacity of swelling and dissolution.¹ Some of them swell to an unlimited extent, lose their form and finally dissolve completely. Other colloids, apparently chemically identical with the first, swell only up to a certain limit. Treated with the same

¹ See e.g. the monographs by J. R. Katz, in *Kolloidchem. Beihe.*, 1917, 9, 1; and *Ergebnisse der exakten Naturwissenschaften*, 1924-25.

solvents as those of the first kind, they retain their form and remain undissolved even after a long treatment with large quantities of the solvent. At the same time, their capacity of swelling may be very extensive; the volume of the substance being increased by swelling to about 50 or 100 times its initial value.

Many natural products with a highly polymeric structure have modifications of these two kinds. We may mention for instance the two modifications of indiarubber. Besides the ordinary, soluble and unlimitedly swelling product, there exists an insoluble modification with a limited swelling capacity.³ The two are known as α - and β -caoutchouc.³ They cannot be distinguished by chemical analysis. In the case of some proteins, too, insoluble forms, with a limited swelling-capacity are known in addition to other modifications—hardly distinguishable from the first by chemical analysis, but soluble and swelling without limit. If such important differences of physical properties occur with substances of relatively low molecular weight, they can usually be traced back to variations in the chemical structure. In the case of the colloids in question, no differences of chemical constitution could at first be detected, and their different behaviour has therefore been described as a "colloidal phenomenon." The explanation of the solubility of the one and the insolubility of the other modification was sought in their different micellar structure rather than in a different molecular constitution, as in the case of low molecular substances.

The investigations of highly-polymeric *synthetic* substances revealed, however, that this point of view cannot be correct. Even in the case of colloids, the variations of the physical behaviour are due to chemical differences in the molecular structure. The "macro-molecules" of the soluble colloid with their unlimited swelling capacity, are different from those of the insoluble colloid of similar composition. The proof given is based, firstly, on experiments with synthetic polystyrenes. A soluble modification of this highly polymeric substance was prepared, in addition to an insoluble one.⁴ Both are products of eucolloidal nature—tough, vitreous substances, which appear to be identical. They both swell with organic solvents—benzene, carbon tetrachloride, carbon disulphide. But whereas the molecules of the first modification are removed from the surface by the action of the solvent—dissolution occurring simultaneously with swelling, the second substance does not dissolve during the swelling and retains therefore its original form, as shown in Plate I, 2. Chemical analysis reveals no difference between the two products, despite their different behaviour to solvents. The two substances *are*, however, different in their chemical constitution (and not, as might be supposed, in their micellar structure). But this difference can hardly be detected by analysis. The difference is revealed by the methods of producing the two modifications synthetically.

The polymerisation of pure styrene⁵ leads to the "polystyrenes," possessing long thread-shaped molecules. The actual length of the

³ C. O. Weber and W. A. Caspari, *Ber. Dt. Chem. Ges.*, 1909, **33**, 779; W. A. Caspari, *J. Soc. Chem. Ind.*, 1913, **32**, 1041; Feuchter, *Kolloidchem. Beihefte*, 1925, **20**, 434.

⁴ P. Bary and E. A. Hauser, *Kautschuk*, 1928, p. 97.

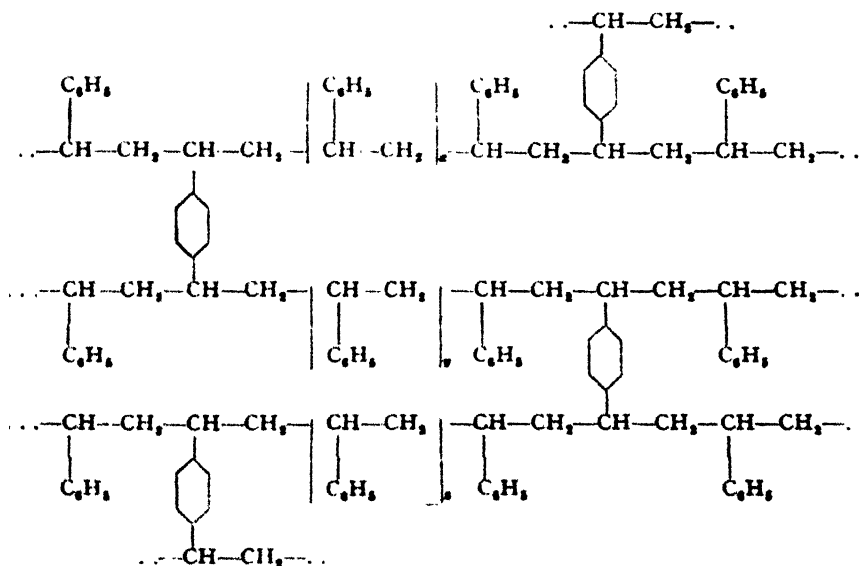
⁵ H. Staudinger and E. Husemann, *Ber. Chem. Ges.*, 1935, **68**, 1618; H. Staudinger and W. Heuer, *Ber. Dt. Chem. Ges.*, 1934, **67**, 1164.

⁶ See H. Staudinger, *Die hochmolekularen organischen Verbindungen, Kautschuk und Cellulose*, Verlag J. Springer, Berlin, 1932, the paper with W. Heuer, p. 157.

threads depends on the conditions of polymerisation: Slow polymerisation at low temperatures gives eucolloidal polystyrenes; their order of polymerisation is not less than 1000 to 5000. Rapid polymerisation with the help of catalysts (for instance, tin tetrachloride) gives hemicolloidal powders, with a degree of polymerisation of not more than 50 or 100. All these products are soluble in organic solvents. The hemicolloids dissolve without swelling, the eucolloidal products swell strongly during the dissolution.

If a small quantity of *para*-divinylbenzene is added to the styrene before polymerisation, and the latter carried out at about 60-100° C. a mixed polymeric product of styrene and divinylbenzene is obtained. Its outer appearance is the same as that of the pure polystyrene prepared under the same conditions: it is a tough, hard glass. But its solubility is quite different: the "mixed" product is insoluble in organic solvents, although it can be swollen by them to a very high degree. The addition of divinylbenzene has thus transformed the soluble polystyrene, with its unlimited swelling capacity, into an insoluble product with a restricted capacity of swelling.

The explanation must be sought in the formation of a kind of divinyl benzene "bridges" linking together the thread-molecules of the polystyrene, as illustrated by the following formula⁶:



As shown by this formula, the "mixed" polymeric substance is composed of macro-molecules extending in all three dimensions, and not of simple thread-molecules, as was the case with the "pure" polystyrene.

The quantity of divinylbenzene which is required to obtain the insoluble product instead of the soluble one, is exceedingly small. One molecule of divinylbenzene is enough for 10,000-50,000 molecules of the monomeric styrene (depending on the conditions of polymerisation). This corresponds to an addition of about 0.01-0.002 per cent. of divinylbenzene—a change of composition which cannot be discovered by ordinary

* H. Staudinger and W. Heuer, *Ber., Dt. Chem. Ges.*, 1934, **67**, 1166.

chemical analysis. It is not surprising, therefore, that the two polystyrenes appear to be identical when studied analytically. It is only by their synthesis that light is thrown on the differences in the structures of the two modifications.

The smallness of the quantity of divinylbenzene sufficient to cause such an important change in the physical properties of the polystyrenes is due to the fact that the soluble polystyrene is composed of very long chain-molecules. It is sufficient to establish some few links between adjoining macro-molecules in order to make a dissolution of the substance impossible. The swelling-capacity remains, because the molecules retain their tendency to form solvates; but even after solvation they cannot leave the bulk of the substance, because they are linked together by the "bridges" formed by divinylbenzene.

Mixed Polymeric Products with Different Concentrations of Divinylbenzene.

After having elucidated the cause of the formation of insoluble polystyrene, we proceeded to the preparation of polystyrenes contain-

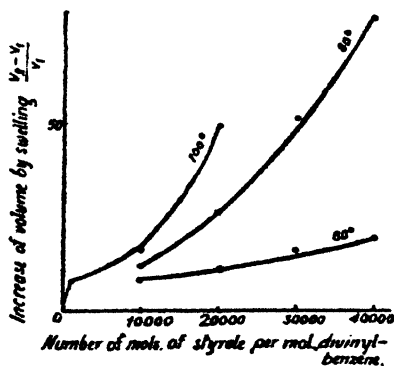
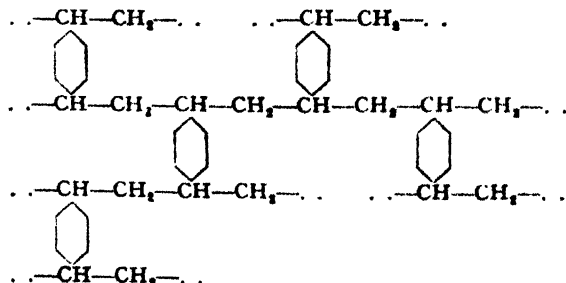


FIG. 1.

ing different proportions of divinylbenzene, in order to investigate the influence of the number of links between the molecular chains on the swelling-capacity of the product. In accordance with our anticipations, we found, as a general rule, a decrease in swelling capacity with increased concentration of divinylbenzene. This is illustrated by Table I. and Fig. 1.

If the concentration of divinylbenzene is higher, products are obtained which hardly show any swelling at all. Pure para-divinylbenzene gives when polymerised at 60-100° C. a product which out-

wardly resembles the polystyrenes obtained under the same conditions. Like eucolloidal polystyrenes, these poly-divinylbenzenes are vitreous substances; but they differ from polystyrenes in that they have no swelling capacity whatsoever. The poly-divinylbenzenes are very brittle and can easily be powdered. This difference of mechanical properties is explained by the building up of poly-divinylbenzenes from three-dimensional molecules, instead of the thread-shaped molecules of the polystyrenes. The structure can be symbolised as follows: ⁷



⁷ H. Staudinger and W. Heuer, *Ber. Dt. Chem. Ges.*, 1934, **67**, 1167.

TABLE I.—SWELLING OF MIXED POLYMERIC PRODUCTS OBTAINED FROM STYRENE WITH VARIABLE AMOUNTS OF DIVINYLBENZENE. SOLVENT: BENZENE.

1. Duration and Temperature of Polymerisation.	2. Number of Mols. of Styrene Per Mol. of Divinylbenzene.	3. Per Cent. of Soluble Poly- styrene Extracted (from the Product).	4. Number of Mols. Benzene Absorbed by 1 Mol. of Styrene.*	5. Increase of Volume $\frac{v_2 - v_1}{v_1}$ by Swelling.
2 months, 60° C.	10,000	—	9.0	7.6
	20,000	10	13.3	11.2
	30,000	19	18.6	15.1
	40,000	23	22.6	19.1
14 days, 80° C.	10,000	10	14.4	12.2
	20,000	27	31	20.2
	30,000	40	59.5	50.4
	40,000	50	92	78.0
	50,000	65	213	181.0
3 days, 100° C.	1,000	—	10.0	8.5
	10,000	19	18.5	15.7
	20,000	40	58	48.9
	30,000	64	260	220

* After deducting the amount of styrene extracted by the solvent.

This is another proof of the close connection between the mechanical stability of the polystyrenes (and similar polymeric products) and the long thread-form of their molecules.

The polymeric products with limited swelling capacity are connected to the pure polystyrenes by a whole series of intermediary forms. When the proportion of divinylbenzene becomes very small, the mixed polymeric substances show a very high swelling capacity and contain at certain amount of soluble polystyrenes, which can be extracted by the solvent without changing the form of the remaining body. A comparison between columns 3 and 5 of Table I. shows that the swelling becomes higher with an increased proportion of soluble matter in the insoluble product.

At still lower concentrations of divinylbenzene, the polymerised product no more retains its form in swelling. The linking of the polystyrene-macro-molecules by divinylbenzene bridges becomes too weak to hold the substance together. If the concentration of divinylbenzene is decreased still further, the whole substance becomes soluble. But even after dissolution, the polystyrene-molecules remain linked to groups by divinylbenzene-links; the average length of the dissolved molecules is therefore greater than in solutions of pure polystyrenes and the viscosity of the solution therefore higher. A polystyrene obtained by polymerisation of pure styrene at 100° C. has for instance a viscosity $\eta_{sp}/c = 21.5$. With a divinylbenzene concentration of 0.0025 per cent., the product obtained under the same conditions is still soluble, but its solution has a much higher viscosity: $\eta_{sp}/c = 41.6$. This indicates clearly that the molecules of the "mixed" polymer are larger than those of the pure polystyrene.

Mixed Polymeric Products with Polystyrene-Chains of Different Length.

We further investigated the connection between the length of the polystyrene-chains and the amount of divinylbenzene required for obtaining an insoluble product. We first polymerised pure styrene under different conditions and determined the length of the polystyrene-macromolecules obtained in different cases. We then polymerised mixtures of styrene and divinylbenzene under the same conditions and determined the smallest amount of divinylbenzene which gave a polymeric product with limited swelling capacity, capable of retaining its form after swelling. Under the conditions in which hemicolloidal polystyrenes were formed, the amounts of divinylbenzene necessary for the polymers to become insoluble were much larger than in the case of eucolloidal products, with their longer chain-molecules. Table II. shows how widely different are the proportions of divinylbenzene under different conditions.⁸

TABLE II.—MINIMUM AMOUNTS OF DIVINYLBENZENE REQUIRED FOR THE PRODUCTION OF A POLYMER WITH LIMITED SWELLING CAPACITY, WITH DIFFERENT LENGTHS OF POLYSTYRENE-CHAINS.

1.	2.	3.	4.	5.	6.	7.
Pure Polystyrene.	Conditions of Polymerisation.	η_{sp}/c .	Order of Polymerisation of the Pure Polystyrene.	Chain-length in Å.	Number of Mols. Styrene per Mol. Divinylbenzene.	Per Cent. Concentration of Divinylbenzene.
Hemicolloid	20 per cent. styrene-solution in benzene + 0.4 per cent. SnCl_4 , at 0°	0.54	30	75	1	55
	Pure styrole + 0.4 per cent. SnCl_4 , at 0°	1.3	70	175	6	17
Mesocolloid	Pure styrene at 200°	4.3	240	600	1,000	0.1
	Pure styrene at 150°	8.9	510	1,275	7,500	0.012
	Pure styrene at 120°	15.1	840	2,100	15,000	0.006
Eucolloid	Pure styrene at 100°	21.5	1,200	3,000	30,000	0.003
	Pure styrene at 80°	30.6	1,700	4,250	50,000	0.002

Table II. shows that no direct *proportionality* exists between the amount of divinylbenzene required for making the product insoluble and the chain-length of the polystyrene. This amount is relatively much higher for hemicolloidal products than for eucolloidal polymers. It is therefore impossible to calculate the length of the polystyrene-chains from the amount of divinylbenzene which makes them insoluble (we hoped first to find in this way a possibility of determining chemically the chain-length of the polystyrenes). Only as a general conclusion can be drawn from these investigations the fact that the polystyrene-chains are very long, since such a small amount of divinylbenzene is sufficient to link them together. The experiments show further, that in the eucolloidal polymers with limited swelling capacity not the whole of the polystyrene molecules are linked together by divinylbenzene-bridges, but

⁸ H. Staudinger and E. Husermann, *Ber.*, 1935, **68**, 1618.

only a part of them. These substances must represent closely interwoven mixtures of three-dimensional macro-molecules of the "mixed" polymer with the thread-molecules of the pure polystyrene.

Swelling in Different Solvents.

In a previous paper⁹ we have shown that the solubility of the polystyrenes is very different for different solvents. There exist a number of solvents, *e.g.*, benzene, carbon disulphide, carbon tetrachloride and tetralin, which dissolve polystyrenes very readily. These are solvents with a tendency to form solvates with the aromatic radicals of the polystyrene molecules as well as with their aliphatic chains. Other solvents, as for instance butyl-acetate or methyl-ethyl-ketone do not form solvates with the aliphatic chains. Cyclohexane and decaline, on the other hand, show affinity to the aliphatic chains only, and do not form solvates with organic radicals. In solvents

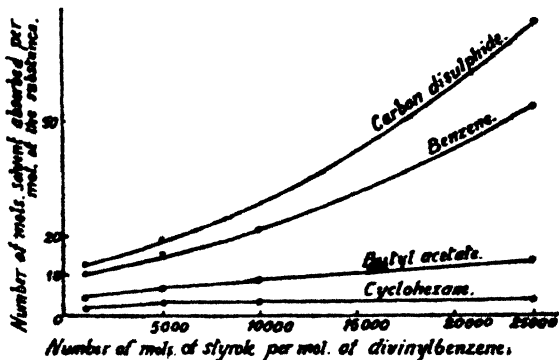


FIG. 2.

of this kind, which only partially solvate the polystyrenes, these substances are soluble to a much lesser degree than in the first mentioned solvents. We have investigated the swelling of the polystyrenes with limited swelling capacity in all these solvents. We found a much stronger swelling in "good" solvents; the swelling was nearly independent of the nature of the solvent, provided that it belonged to this group. In solvents of the second kind, the swelling was much weaker, especially in cyclohexane, which forms solvates with aliphatic chains only. In comparing the swelling of different polystyrene preparations with variable concentrations of divinylbenzene, in different solvents, we found that all of them behaved in the same way. This is shown by Table III. and Fig. 2.

TABLE III.—INCREASE IN VOLUME $\frac{v_2 - v_1}{v_1}$ BY SWELLING OF "MIXED" POLYMERS OF VARIABLE COMPOSITION IN DIFFERENT SOLVENTS.

Mols. Styrene per Mol. Divinylbenzene.	CS ₂ .	C ₆ H ₆ .	CCl ₄ .	Tetralin.	Butyl-acetate.	Methyl ethyl ketone.	Decaline.	Cyclo-hexane.
1,000 I. . .	8.0	8.6	8.5	8.3	5.5	3.4	2.5	1.2
1,000 II. . .	—	8.9	—	10.0	—	—	2.9	1.7
5,000 . . .	10.7	14.1	16.0	11.4	9.1	4.6	6.2	2.8
10,000 I. . .	20.3	19.6	20.6	21.6	11.6	6.6	11.1	2.9
10,000 II. . .	19.0	18.8	20.0	18.0	9.8	7.4	8.6	2.3
25,000 . . .	40.0	45	—	28	17.5	12.5	13.5	2.5

⁹ H. Staudinger and W. Heuer, *Zeit. physikal Chemie.*, 1934, 171A, 129.

We also showed in a previous paper that the specific viscosity of a polystyrene in "good" solvents is independent of the nature of the solvent. In "bad" solvents we found values of η_{sp}/c which were generally much smaller. The numbers are given in Table IV. for two different polystyrenes.

TABLE IV.— η_{sp}/c VALUES FOR TWO POLYSTYRENES IN DIFFERENT SOLVENTS ($c = 0.02$ mols. per litre = 0.2 per cent.)

Polystyrene. Mol. Weight.	CS ₂ .	C ₆ H ₆ .	CCl ₄ .	Tetralin.	Butyl- acetate.	Methyl ethyl ketone.	Decaline.	Cyclo- hexane.
60,000 .	9.1	10.9	9.3	9.8	6.0	5.1	5.8	1.8
140,000 .	23.9	27.9	25.4	26.5	14.9	9.4	9.6	insoluble

A comparison between Tables III. and IV. shows that the viscosity of polystyrenes in solution is closely connected with their swelling capacity. The explanation is that swelling capacity, solubility and viscosity all ultimately depend on the strength of solvation of the molecules of polystyrene by the corresponding solvent.

Soluble and Insoluble Caoutchouc ; Synthetic Caoutchouc.

It is well known that the ordinary, soluble and unlimitedly swelling caoutchouc, when stocked for a long time, is transformed into an insoluble caoutchouc with limited swelling capacity. It can be made soluble again by mastication. It was therefore supposed that the transformation of the soluble caoutchouc into the insoluble one was a reversible process.¹⁰ Subsequent investigations revealed, however, that this transformation of the " α -caoutchouc" into the " β -caoutchouc" occurs only in presence of oxygen¹¹ and the long chain-molecules of the α -form are converted into three-dimensional molecules of the β -form by oxygen-links between the chains. By masticating the insoluble caoutchouc, the three-dimensional molecules are broken-up;¹² at the same time, the chains are shortened by oxidation. The "regenerated" soluble caoutchouc is therefore a highly degraded product; the order of polymerisation of its molecules is not greater than 300-500, as against 1000-2000 of the original product. The transformation of the soluble caoutchouc into the β -modification is thus not a reversible colloidal process, but an irreversible change in the chemical structure of the macromolecules.

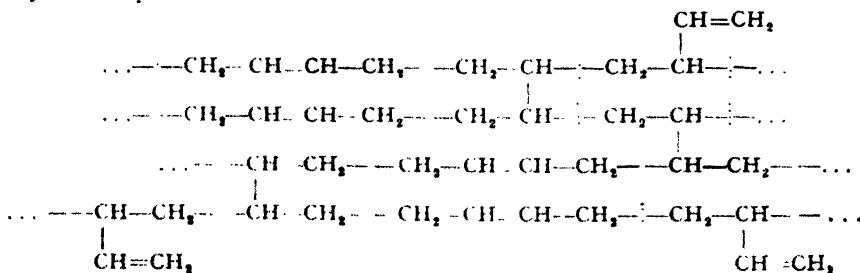
The polymerisation of butadiene leads sometimes to soluble, sometimes to insoluble products. The soluble synthetic caoutchouc is composed of single thread-shaped molecules. Our experience with polystyrenes led us to assume that the insoluble synthetic product is distinguished from the soluble one by the existence of links between the single threads. The more complicated molecular structure of the synthetic isoprene caoutchouc as compared with the natural product has

¹⁰ P. Bary and E. A. Hauser, *Kautschuk*, 1928, 97.

¹¹ H. Staudinger and H. F. Bondy, *Liebigs-Annalen*, 1934, 488, 153; H. Staudinger and E. O. Leupold: *Die hochmolekularen organischen Verbindungen-Kautschuk und Cellulose*, p. 443.

¹² H. Staudinger and W. Heuer, *Ber. Dt. Chem. Ges.*, 1934, 67, 1159.

been established previously by experiments of degradation with ozone. The butadiene-caoutchouc certainly has a very irregular structure, because its ozonisation yields only a very small quantity of succinic acid (which could be expected to be formed in great quantities if the structure were regular). Furthermore, the catalytic reduction of this kind of synthetic rubber leads to easily soluble high-molecular paraffins. Since high molecular normal paraffins are insoluble or only slightly soluble, these reduction-products must have molecules with side-chains.¹³ This points to the existence of branched chains in the polymeric butadiene itself. We may suggest the following diagrammatic formula of this synthetic product : ¹⁴



Thus, in the case of caoutchouc, also the difference between the modification with limited and the one with unlimited swelling capacity is based also on different molecular structures.

Biological Significance of these Experiments.

The above-described experiments permit the general conclusion that colloids with limited swelling capacity are composed of long thread-molecules, linked together by some kind of "bridges" to three-dimensional molecules. The longer the threads and the smaller the number of links the higher the swelling capacity of the molecular colloid. The number of atoms in the links is exceedingly small as compared with their number in the chains; despite this small proportion, the existence of the links changes completely the physical properties of the colloid, especially in regard to its solubility. The only substances liable to change their physical properties (and sometimes their chemical behaviour as well) by such minute changes in their structure are those of extremely high molecular weight.¹⁵ All changes in the properties of organic substances are based on changes in their molecules. If a substance has molecules of a small molecular weight, every atom or group added to it will appreciably change its composition, and the addition can be detected by ordinary chemical analysis. The position becomes different, where highly-polymeric molecules are concerned. A very slight change in the structure of the macro-molecules can lead to a very important change in properties, as we have seen in the cases discussed above. The corresponding changes in the composition of the

¹⁸ The influence of side-chains on solubility is discussed by H. Staudinger and E. O. Leupold, *Helv. chim. acta*, 1931, **18**, 224.

¹⁴ H. Staudinger and W. Heuer, *Ber. Dt. Chem. Ges.*, 1934, **67**, 1172.

¹⁵ Compare for instance the completely different behaviour of α - and γ -polyoxymethylenes, H. Staudinger and collaborators, *Liebigs Annalen*, 1929, 474, 159; and H. Staudinger, *Die Bedeutung der Erforschung hochpolymerer Stoffe für die Biologie*, in *Zangger-Festschrift*, Rascher, Zürich, 1934.

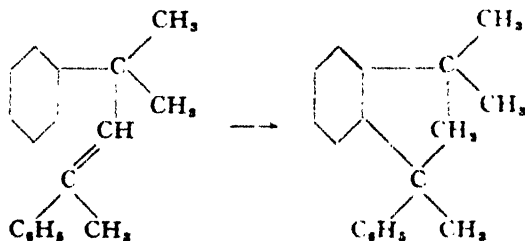
macro-molecule may be so small that they escape detection by analytical methods. Only a happy chance permits us to recognise the existing differences in structure of the macro-molecules as in the case of polystyrene, where we are able to prepare the corresponding polymeric substances synthetically.

Many substances of great biological importance are of highly-polymeric structure—proteins being the most important example. We may expect that in these cases, too, a minute change of composition may lead to important changes in physical properties. A slight change in the composition, hardly detectable analytically, may, for instance, convert a soluble protein into an insoluble one. The experiments on polystyrenes, which form the main subject of this paper, may therefore acquire some biological interest, as analogies to biologically important reactions.

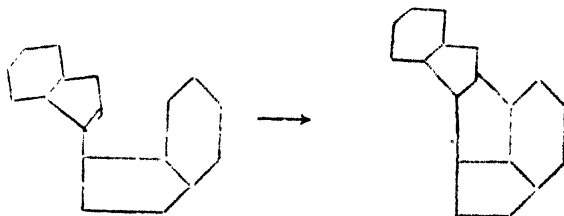
GENERAL DISCUSSION.

Mr. N. J. L. Megson (*Teddington*) said: The effect of small quantities of divinylbenzene in bringing about insolubility of polystyrene, reported by Professor Staudinger, recalls the hardening of soluble "Novolak" resins by small proportions of formaldehyde. This hardening may be attributed to cross-linking of phenol-methylene chains by methylene groups (involving in this case, elimination of water). Before final insolubility and infusibility are attained, the resin passes through the so-called "B" stage, when the material swells in acetone, but is insoluble.

Dr. E. Bergmann (*Rehoboth*) said: The paper mentions that the unsaturated di-indene is converted by heating into a saturated isomer. Now, the usual reaction of unsaturated dimers, *e.g.* in the case of dimeric α -methylstyrene



is impossible in the case of di-indene on stereochemical grounds, the expected substance



hardly being stable. Is not the so-called saturated dimer identical with truxene? The question seems a plain organic one, but the above cyclisation reaction may be of importance, since it provides one of the possible chain-breaking mechanisms.

Professor H. I. Waterman (*Delft*) said: Speaking also in the name of J. C. Vlугter, we direct attention to Table V. of G. S. Whitby's paper, in which a number of atoms of bromine added after a period of one day is

1.10, after three days 1.82, and after four days 2.00. We do not agree with the conclusion that "had a longer period of absorption than twenty-four hours in analogous experiments been given the bromine addition of all samples would have been equivalent to two atoms per mole."

Our experience is that the bromine addition values generally do not give good results for polymerised unsaturated hydrocarbons of higher molecular weight. In this connection, we ask the opinion of Professor Staudinger because it was a paper of Staudinger and Steinhöfer which was cited in Whitby's work.

Staudinger found that the addition of very small quantities of divinyl benzene caused the formation of insoluble styrene polymers. We think that this is a very important experiment which may find application in industrial work. On the other hand, this and analogous experiments prove that the viscosity of such systems of styrene polymers will depend very much on the presence of impurity, even though only traces of impurities are present.

Professor H. Staudinger (Freiburg i. Br.) said: Mr. Whitby states that the polystyrenes contain double bonds at the end of the molecule, the number of which can be determined by bromine titration. In this way he claims to be able to estimate the molecular weight of polystyrene by an end group determination. Mr. Waterman has asked me whether or not corresponding observations have been made at the Freiburg laboratories, since Mr. Whitby quotes the work of A. Steinhöfer¹⁶ as a proof for his point of view. Dr. Waterman is of the opinion that in the case of high molecular unsaturated compounds the addition of bromine proceeds only very slowly, and the amount of added bromine cannot be determined accurately enough. The observations of A. Steinhöfer and of M. Brunner¹⁷ agree absolutely with this conception. With increasing time of reaction the bromine addition increases more and more, and a marked end point of the reaction, particularly in the case of higher molecular weight compounds, cannot be noticed. However, one can determine the amount of bromine which is taken up by substitution through the determination of the amount of eliminated hydrogen bromide. Even in the case of hemicolloidal polystyrenes the molecular weights from the bromine titration method do not agree with the values obtained by the cryscopical and viscosimetric methods. In other words, it is not possible to decide definitely whether or not the hemicolloidal polystyrenes bear a double bond at the end of the thread molecule, and take up one bromine molecule per double bond.

Professor K. H. Meyer (Genève) said: If Professor Staudinger says that the variation of the solubility of natural substances of apparently identical chemical composition is to be generally explained by their different micellar structure rather than by a different molecular constitution, he will remember that we advanced the explanation by cross linkings, as early as 1928 and 1929.¹⁸ We discussed in a general way the effect of cross linkings on the physical behaviour, of both synthetic and natural material. The theory now generally adopted, that the physical effect of vulcanisation is due to the chemical *Vernetzung* (formation of a three-dimensional network) was a result of these considerations.¹

Very often natural products are rendered soluble by some chemical treatment or by boiling (e.g., collagen-gelatin). The nature of the chemical cross linkings cannot be established by analysing and comparing the soluble and the insoluble product, as Staudinger emphasises, in view of the minute quantities of these bindings. But their nature can be revealed by kinetic investigations. The temperature coefficient of the reaction (i.e., the transformation of the insoluble into the soluble product) and the

¹⁶ H. Staudinger and A. Steinhöfer, *Liebigs Annalen*, 1935, 517, 42.

¹⁷ M. Brunner, *Dissertation*, Zurich, 1926.

¹⁸ *Ber.*, 1928, 61, 1947; *Bioch. Z.*, 1929, 208, 23. Meyer-Mark, *Aufbau der Hochpolymeren* 1930, 74 and 227; cf. also Sheppard and Houck, *J. physical chemistry*, 1930, 34, 273.

influence of added chemicals can elucidate the nature of the reaction and of the bridge, which is split up (e.g., the bucking of cellulose, the transformation of collagen into gelatin, of insoluble into soluble starch).

Not only chemical homeopolar bridges, but also bridges of dipole-forces or other weaker forces, may be the cause of the phenomenon of limited swelling. If, for instance, some OH or C=O groups are attached to a high molecular hydrocarbon soluble in benzene, they combine with other similar groups of other macromolecules to form quadrupoles, and these cross linkings are not split up by apolar solvents. The following is a very characteristic example: Natural rubber is imperfectly soluble in benzene. The insoluble part (so-called "gelcautchouc") is rendered soluble in the cold by addition of some butyl alcohol, a fact well known in the rubber industry. The explanation is, that the quadrupole linkings which are due to the presence of very few oxygen or nitrogen atoms in the molecule and which form the network, are solvated and split up by the polar solvent.

Dr. F. C. Wood (*Manchester*) said: The effect described with polystyrene and a small quantity of divinyl benzene has an exact parallel in cellulose chemistry where a small quantity of formaldehyde fixed to regenerated cellulose (as methylene ether) converts a swellable fibre, soluble in cuprammonium hydroxide, into a non-swellable fibre insoluble in this solvent.

The explanation of this was suggested to me many years ago by Mr. H. J. P. Venn, and the same explanation was published by Meunier and Guyot in 1929 on similar lines to those now used by Professor Staudinger.

Professor H. Staudinger (*Freiburg i Br.*) said: I am obliged for the mention of further examples of limited swelling colloids, which, it is justifiable to assume, are built up of thread molecules linked by chemical cross linkages so as to form three-dimensional macromolecules.¹⁹ The case of the insoluble polystyrenes described in my paper differs from the above mentioned in that, in the polystyrenes, a controllable preparation of a limited-swelling colloid is possible and in that it is further possible to examine the differences in the properties of such limited-swelling colloids, firstly, as a function of the chain length of the macromolecules and, secondly, of the number of cross linkages. Thus it was possible to obtain an accurate insight into the structure of the limited swelling colloids.

In this case very small amounts of divinyl benzene can link the linear macromolecules so as to form still larger insoluble molecules. Therefore Mr. Waterman is justified in asking whether reliable conclusions about the length of the molecules can be drawn from the viscosity measurements, since indeed traces of impurities can bring about such a linking of the chain molecules. In answer to this I would like to point out, as has been done,²⁰ that a determination of the length of the molecules is possible by the viscosity measurements; that is, we determine a magnitude which is important for the characterisation of the physical properties of the substance. However, by this method we cannot ascertain whether single chain molecules or molecules of a more complicated structure, e.g. branched molecules, are present. In order to solve this question we must investigate whether the molecular weight obtained from viscosity measurements agrees with the values obtained by the osmotic method, because such an agreement will be observed only in the case where unbranched thread molecules are present.

Professor Meyer mentions that insoluble rubber (i.e. rubber in which the thread molecules are linked to each other by oxygen cross linkages, thus forming three-dimensional macromolecules) can be dissolved by merely treating it with butyl alcohol, but it should be ascertained whether the solvent was completely free from oxygen, for very small amounts of oxygen are sufficient to break down the thread molecules. This degradative effect of oxygen could render insoluble rubber soluble, since the three-

¹⁹ Compare H. Staudinger, *Z. ang. Chem.*, 1929, 42, 72.

²⁰ *This vol.*, paper v.

dimensional macromolecules are changed back into thread molecules.²¹ Of course, linkage of thread molecules may be effected not only by primary bonds but also by molecular attraction forces. Three-dimensional coordinative macromolecules of such a structure are, of course, much more unstable than three-dimensional normal macromolecules.

In regard to the swelling of high molecular weight products we must discriminate between the swelling of organised substances (e.g., natural cotton fibres) and that of substances prepared from those. The swelling of the natural cotton fibre and other natural fibres can proceed differently from that of the high molecular weight cellulose prepared from these fibres.²² The reason for this is that the naturally grown substance has an internal structure different from that of the material obtained from it by further chemical treatment. But if one wishes to understand the swelling of organised substances (e.g. of natural cotton fibres) this phenomenon must be first elucidated with the substance of these fibres, the cellulose itself.

Professor G. S. Whitby (Ottawa), in reply, said: In discussing the occurrence of unsaturation in chain polymers and its extent, my concern was not exactly, as the remarks of Professors Watermann and Staudinger suggest, to deduce the molecular weight from the degree of unsaturation, but, rather, assuming the molecular weight to be reliably known by cryoscopy, to deduce the extent of unsaturation per mole. I agree that the measurement of the bromine additive capacity of highly polymerised hydrocarbon molecules is, because of experimental difficulties, by no means as exact or conclusive a method of determining the extent of unsaturation as could be wished. At the moment it is, however, the best method for which data are available. And such data considered qualitatively clearly establish the fact that the polymeric molecules *are* unsaturated and considered quantitatively suggest that the extent of the unsaturation corresponds to one double bond per molecule, irrespective of the molecular size.

After all, there would seem in the general case to be only three ways in which it is possible to resolve the indeterminateness involved in the current practice of writing the formulae of long-chain polymers with free terminal valencies (as, e.g., $-\text{[CHPh} \cdot \text{CH}_2\text{]}_n-$). The first possibility is to suppose that ring formation occurs. Against this is not only the lack of experimental evidence but the fact that, since highly polymeric products are usually mixtures representing widely different degrees of polymerisation, it is necessary to believe that a large number of rings of very different sizes (containing, say, 20, 22, 24, 26 . . . 100 . . . carbon atoms) are capable of forming with substantially the same degree of ease. The second possibility is to suppose that the terminal valencies are satisfied by "foreign" elements or groups, derived, not from the polymerisant, but from the medium. Staudinger has found such groups to be present when formaldehyde is polymerised in the presence of water. In this case, however, not a true polymerisation process but a condensation polymerisation process (to use the terms employed by Professor Staudinger in his discussion of Dr. Carothers' paper) is involved, each molecule of formaldehyde or at least one molecule per chain reacting as $\text{OH} \cdot \text{CH}_2 \cdot \text{OH}$.²³ No evidence has been secured, despite a search for it, of the occurrence of "foreign" end groups in the products of true polymerisation processes, and, indeed, since in such cases pure chemical substances polymerise or can be caused to polymerise without the intervention of chemical reagents or a reaction medium, it seems *a priori* unlikely that foreign end groups can enter in. There remains then the third possibility, *vis.* the occurrence of a terminal double bond. Since this has not the *a priori* unlikelihood of the first two possibilities, it must be given serious consideration, and, as I tried to indicate, is not in fact without experimental support.

²¹ Compare H. Staudinger and H. F. Bondy, *Liebigs Annalen*, 1931, 488, 153; H. Staudinger and E. O. Leupold, *Die hochmolekularen organischen Verbindungen, Kautschuk und Cellulose*, Berlin, 1932, p. 442.

²² Compare H. Staudinger, *Naturwissenschaften*, 1934, 817.

²³ Cf. Staudinger, *Die hochmolekularen organischen Verbindungen*, 1932, 255.

ALDEHYDE PHENOLIC CONDENSATIONS FROM A CHEMICAL STANDPOINT.

BY N. J. L. MEGSON.

Received 2nd August, 1935.

Both crystalline and resinous products resulting through condensations of formaldehyde with phenols have been known for many years, and it is common knowledge to what extent phenolic resinoids have dominated the field of synthetic resins since their first commercial exploitation in 1908 by Dr. L. H. Baekeland and others. It is nevertheless true, that of all resins manufactured industrially to-day, least is understood of the structure of these phenolic materials. This position is brought about, partly, because the immediate requirements of industry have been satisfied without the necessity of a great deal of fundamental research, and, partly, because of the difficulties encountered by early investigators in the elucidation of substances as intractable as hardened resinoid.

It is only since 1925, when Baekeland and Bender published their well-known paper,¹ which contained a comprehensive summary of previous work, that systematic study has been made of the problem. Until that date, assignment of structure to account for known properties was largely guesswork. The knowledge that acidic condensations of phenols with formaldehyde generally led to compounds of dihydroxydiaryl-methane type, and that alkaline condensations produced phenolic alcohols, was linked with the facts that acidic condensations frequently led to permanently fusible and soluble resins (Novolaks), and that condensations under alkaline conditions generally led to heat-hardening resins ("Bakelite" type). Early speculations by Raschig² suggested that Novolaks were mixtures of dihydroxydiarylmethanes with phenolic alcohols and free phenol, the isomerism possible in these compounds being responsible for the resinous state, and rendering difficult isolation of individual constituents.

It is intended in the present communication to deal with certain aspects of Novolaks as revealed by chemical examination of their constituents. Such resins may be regarded as intermediates in the production of resinoids, and knowledge of their structure would assist substantially the elucidation of many problems associated with the more complex material.

Despite the difficulty of disproving the conclusions of Baekeland and Bender, who regarded Novolaks as best represented by a phenoxy-hydroxyphenylmethane structure, present views incline to Scheme I., which satisfactorily explains the formation of the fusible, soluble type of resin.

¹ L. H. Baekeland and H. L. Bender, *Ind. Eng. Chem.*, 1925, 17, 225.

² Raschig, *Z. angew. Chem.*, 1912, 25, 1945.

SCHEME I.

1. $R.OH + CH_2O \rightarrow HO.R'.CH_2OH$ (phenolic alcohols)
- 1a. $R.OH + xCH_2O \rightarrow HO.R^x.(CH_2OH)_x$ (phenolic polyalcohols).
2. $HO.R'.CH_2OH + R.OH \rightarrow HO.R'.CH_2.R'.OH + H_2O$
(dihydroxydiarylmethanes).
3. $HO.R'.CH_2.R'.OH + CH_2O \rightarrow HO.R'.CH_2.R''.(OH).CH_2OH$
(alcohol of dihydroxydiarylmethanes).
4. $HO.R'.CH_2.R''.(OH).CH_2OH + R.OH \rightarrow$
 $HO.R'.CH_2.R''.(OH).CH_2.R'.OH$ (trinuclear compound).
5. In general :—
 $x.R.OH + (x-1)CH_2O \rightarrow HO.R'.CH_2.R''(OH).CH_2)_{x-2}.R'.OH$
(polynuclear chain compound) + $(x-1)H_2O$

Essentially, the process consists of the entry of formaldehyde into phenolic nuclei to form alcohols, followed by condensation with more phenol. The polynuclear chain compounds cannot be called polymerides, since their production involves elimination of water, and they are not reversible. It is not considered that a Novolak can be represented by any one particular polynuclear compound; it will be made up of a complex mixture of such compounds, and possibly their alcohols, and its molecular weight will be the mean value of the molecular weights of its constituents. This complexity is increased by the presence of numerous isomerides of the polynuclear type of substance,⁵ the only phenols in which this type of complexity does not arise being certain of those which contain but two or less *o-p*-positions available for substitution (*e.g.* *p*-cresol, *m*-2-xylene). Such a complex mixture will form a system in which crystallisation of individuals will be difficult, and hence the resinous state will be the stable one. Raschig,³ and later Blumfeldt,⁴ came close to the truth in their speculations, which were, however, made at a time when reliable experimental evidence was not available.

The experimental evidence on which the adoption of Scheme I. is based, can be summarised as follows :—

(a) The isolation of crystalline compounds of phenolic alcohol,⁵ dihydroxydiarylmethane,^{6,7,8} and related types from acidic resinous condensations.

(b) The practical realisation of step 2, involving condensation of phenols with phenolic alcohols to give dihydroxydiarylmethanes.^{6,7,9}

(c) The preparation of polynuclear compounds and their alcohols from *p*-cresol-formaldehyde condensations (Koebner⁹).

(d) Molecular weights, which were shown by Koebner to increase with increased proportion of formaldehyde, whereby longer chains would be expected because the available methylene groups approached the phenolic nuclei in number. Koebner obtained molecular weights for phenol Novolaks as low as 200, confirming Raschig's idea that the resins may consist of comparatively simple mixtures of isomerides.

(e) Estimation by Pollak and Riesenfeld¹⁰ of substances eliminated during resin formation (*e.g.*, uncombined phenol, formaldehyde and

⁵ N. J. L. Megson, *J.S.C.I.*, 1933, 52, 420T.

⁶ A. E. Blumfeldt, *Chem. Ztg.*, 1929, 53, 493.

⁷ L. H. Baekeland, *Ind. Eng. Chem.*, 1912, 4, 737.

⁸ N. J. L. Megson and A. A. Drummond, *J.S.C.I.*, 1930, 49, 251T.

⁹ G. T. Morgan, and N. J. L. Megson, *J.S.C.I.*, 1933, 52, 418T.

¹⁰ Trautenberg, *Z. angew. Chem.*, 1923, 26, 515; Coster van Voorhout, *Chem. Weekblad*, 1920, 17, 2; L. H. Baekeland, *Ind. Eng. Chem.*, 1913, 5, 506; and others.

¹¹ B. A. S. F., *D.R.P.*, 301,451; M. Koebner, *Z. angew. Chem.*, 1933, 46, 251 (*cf.* Koebner, *Chem.-Ztg.*, 1930, 54, 619).

¹² F. Pollak and F. Riesenfeld, *Z. angew. Chem.*, 1930, 43, 1129.

water of condensation), followed by molecular weight determinations. These workers concluded that Novolaks consisted of seven phenolic nuclei united by six methylene groups. Experimental conditions appear to affect this result since repetition of the work by the author yielded resins of appreciably lower molecular weights (350-500 against 522).

(f) Ultimate analyses of resins, which although of little value for assigning actual formulæ, serve as a check on the type of molecular structure involved.¹¹

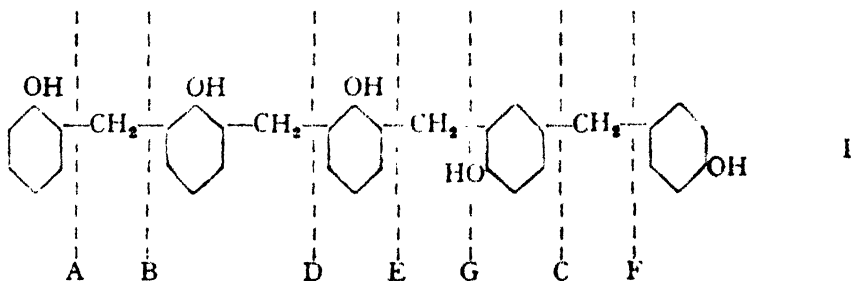
(g) Examination of derivatives of resins, such as acetyl, benzoyl and benzyl.¹¹

(h) Absorption spectra and refraction experiments¹² which imply the persistence of phenyl-methylene chain compounds in resinoids produced under alkaline conditions, and presumably therefore their presence in Novolaks.

(i) Alkaline hydrolysis of resins under pressure to give phenolic homologues.¹³

Further evidence is now presented in support of Scheme I, based on the nature and yields of products obtained by vacuum distillation and pyrolytic decomposition of Novolaks. An implication from Koeber's molecular weight determinations, that yields of lower condensation products decrease with increased formaldehyde concentration, is confirmed by direct isolation of certain compounds.

It is possible to predict what products would be obtained from the degradation of Novolaks, on the assumption that the latter may be regarded as extended dihydroxydiarylmethanes. Consider a constituent of a Novolak prepared from phenol, in which random *o*-*p*-substitution is assumed :—



Decomposition of this compound by heat may cause splitting in various ways. If rupture takes place at A, phenol will be broken off from the end of the molecule, but if it occurs at B or C, *o*- or *p*-cresol should result. If breaking takes place at A and D simultaneously, *m*-2-xenol should be produced, and similarly splitting between E and F should yield *m*-4-xenol. Another case arises, should decomposition occur simultaneously at B and E; a dihydroxydiphenylmethane would be formed, which according to its stability might distil as such, or decompose to give phenols, or lose water between hydroxyl groups to give volatile xanthene, which is the only form in which 2 : 2'-dihydroxydiphenyl-

¹¹ A. Vansheidt, *et al.*, *Plasticheskie Massy*, 1934, No. 3, 17.

¹² A. Schmid and G. de Senarclens, *Helv. Chim. Acta.*, 1933, 16, 10; J. H. de Boer, R. Houwink and J. F. H. Custers, *Rec. trav. chim.*, 1933, 52, 709; R. Houwink, *Brit. Plastics*, 1934, 6, 100.

¹³ I. Allen, Jr., V. E. Meharg and J. H. Schmidt, *Ind. Eng. Chem.*, 1934, 26, 663.

methane exists. If, furthermore, cross-linking of long chains be assumed possible, mesitol could theoretically be produced.

The substances which would be anticipated from other phenolic condensations can be deduced in a similar manner, such substances depending generally on the *o-p*-rule of substitution which limits the number and type of phenols and xanthenes possible.

It should be noted, that an analogous structure based on the phenoxy hypothesis of Baekeland and Bender, would be likely to yield phenols and xanthenes only if, as a result of heating, immediate transformation to the phenolic type of chain, occurred.

The isolation of various phenols and xanthenes from the degradation products of Novolaks, in agreement with the above deductions, has now been achieved, and information thereby becomes available as to nuclear positions occupied by methylene groups.

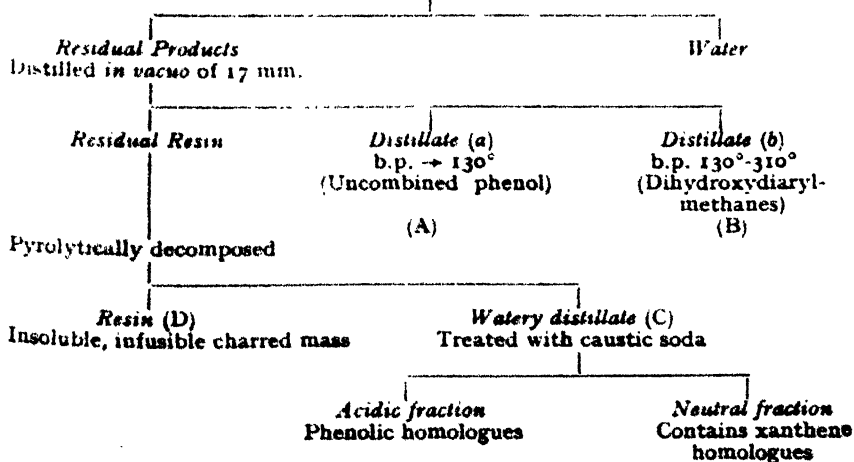
General Experimental Method.

The method by which condensations were examined is given in Scheme II. Condensations were carried out with phenols and aqueous formaldehyde in presence of acid until permanent turbidity at 100° first appeared. The mixture was cooled, the supernatant liquid decanted, and the bottom layer washed repeatedly with hot water to remove catalyst, excess formaldehyde, and water-soluble uncombined phenols. The resulting resin was heated to remove water, and a little steam-distilled phenol, and was then distilled under a pressure of about 15-17 mm. The first distillate was almost entirely uncombined phenol, (A), and the second was a nearly colourless glass, consisting chiefly of dihydroxydiarylmethane isomerides (B). Immediately signs of decomposition appeared, distillation was stopped and the residual resin was decomposed by heating strongly (up to 450° in the resin) at normal pressures, until all distillation ceased. The watery distillate (C), which was accompanied by inflammable vapours whose nature was not determined, contained acidic and neutral materials, separable by caustic soda. The acidic fraction was a mixture of phenols, made up of the original phenol with certain of its methyl homologues, and the neutral fraction contained substances of xanthene type.

SCHEME II.

CONDENSATION PRODUCT.

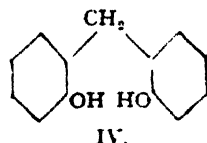
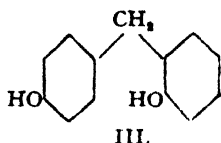
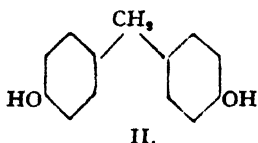
Top layer decanted. Resin washed several times with hot water. Distilled at normal pressure.



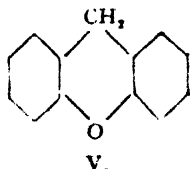
The products of condensation, after preliminary distillation of water, were invariably resinous in character, and despite the high percentage of dihydroxydiarylmethanes frequently present in them, deposited crystals only very slowly. The amount of coke-like residue (D) left after destructive distillation, increased in yield with increase of formaldehyde.

Examination of condensation products derived from phenol, *o*-, *m*- and *p*-cresols and *m*-5-xyleneol has been carried out. A more detailed publication of the results discussed below, will be made in a later communication.

Phenol should theoretically produce three dihydroxydiphenylmethanes,



of which II. and III. are known and have been isolated from resinous condensations. There appears, from previous work,⁴ to be a connection between time of condensation and yield of III., the latter apparently functioning more truly than does II. as an intermediate in resin formation. Vacuum distillation of phenol resin has now given high yields of mixed II. and III. (for low proportions of formaldehyde), with the former slightly preponderating. With increase of formaldehyde through the proportions 0.5, 1.0, 1.5 and 2.0 mols. per mol. of phenol, the yields of fraction (B) were 45 g., 26 g., 20 g. and 0 g. respectively. IV. is not known, but exists in a dehydrated form as xanthene, V.



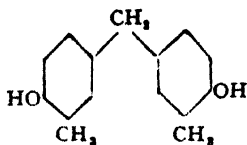
Xanthene has never been identified in phenol resins, which are invariably completely soluble in caustic soda.

Consideration of formula I. has already shown that degradation of phenol resins may yield phenol, *o*- and *p*-cresols, *m*-2- and *m*-4-xyleneols and mesitol, in addition to xanthene. The author has been able to identify only phenol, *o*- and *p*-cresols in the acid fraction of the decomposition products (C), which increased through 12.5 g., 18 g., (17 g.), and 35 g. with increase of formaldehyde through 0.5, 1.0, 1.5 and 2.0 molecules respectively. The small yield of *p*-cresol, compared with that of *o*-cresol, suggests that *p*-substitution is of less frequent occurrence than *o*-substitution, but the observed preponderance of II. over III. contradicts this conclusion. It is possible, either that decomposition takes place more readily at *o*- than at *p*-linkages, or that the resin itself contains a high proportion of *o*-linkages, brought about by continued condensation of III. in preference to II.

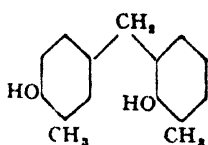
The neutral decomposition products apparently contained xanthene and methyl homologues. The production of these homologues is understandable if splitting of the long chain compound I. takes place at A and G simultaneously, with subsequent or coincident elimination of water between hydroxyl groups.

Phenol resins were more difficult to deal with than others examined, owing to their tendency to pass over to the "gel" stage during vacuum distillation. This tendency is probably due to ready formation of cross-linked compounds, which are not produced so easily in higher phenols owing to steric hindrance effects of methyl substituents.

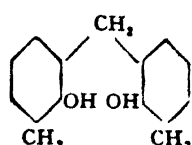
o-Cresol should form three dihydroxyditolylmethanes:



VII.



VIII.

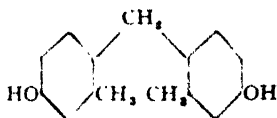


IX.

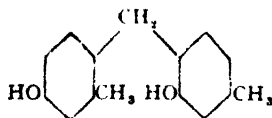
Only VII. is known and has been isolated from *o*-cresol-formaldehyde condensations.⁶ By elimination of water between hydroxyl groups, VIII. should yield 4:5-dimethylxanthene. The phenols produced by pyrolysis should be, *o*-cresol, *m*-2- and *m*-4-xyenols and mesitol.

The only crystalline condensation product obtained from this phenol was VI. in high yield (38 g. from 108 g. of *o*-cresol). No indication of VII. or VIII. was found, and the resin remaining after vacuum distillation was so small (8 g.), that pyrolysis was not proceeded with. Nearly identical results were obtained when formaldehyde was increased from 0.5 mols. to 1.0 mols. It appears that substitution in this condensation takes place almost entirely *p*- to the hydroxyl group, an observation which may be connected with the known difficulty of producing *o*-cresol resins possessing high melting-point, or rapid heat-hardening characteristics.

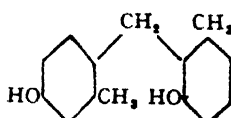
m-Cresol, because of its asymmetry, theoretically forms a more complicated series of condensation products than any other of the methyl phenols; there are, for example, no less than six possible dihydroxyditolylmethanes:



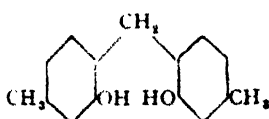
X.



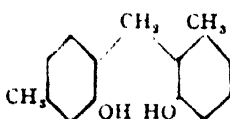
XI.



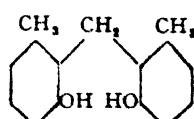
XII.



XIII.



XIV.



XV.

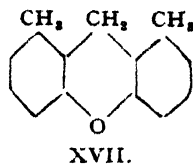
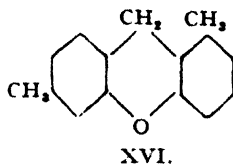
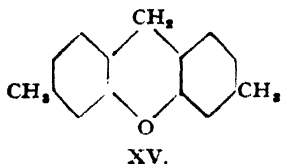
Of these only two have previously been reported, m.p. 161°⁶ and m.p. 113°¹⁴ respectively, both of which were separated from cresol-formaldehyde condensations. The author has now isolated two more *isomerides*, m.p. 99° and m.p. 134°, from the products of vacuum distillation (B), but the orientation of none of these compounds is known.

The substance melting at 99° was crystallised from light petroleum, b.p. 60/80°, in microscopic needles. (Found: C 79.1 per cent., H 7.13 per cent.; $C_{18}H_{18}O_2$ requires C 78.9 per cent., H 7.02 per cent.) *Tetra-bromo-derivative*: Found: Br 57.7 per cent.; $C_{18}H_{18}O_2Br_4$ requires Br 58.8 per cent. The isomeride melting at 134° crystallised from benzene-petroleum in rosettes of spears (Found: C 78.9 per cent., H 6.88 per cent.; $C_{18}H_{18}O_2$ requires C 78.9 per cent., H 7.02 per cent.). (All above are microanalyses.)

The yields of fraction (B) constituted 35 per cent., 24 per cent., 18 per cent. and 11 per cent. respectively, of the dry resin, for 0.5, 1.0, 1.5 and 2.0 molecular proportions of formaldehyde. Uncombined *m*-cresol (A) decreased through the yields; 32 per cent., 16 per cent., 12 per cent., — per cent.

¹⁴ W. C. Harden and E. E. Reid, *J. Am. Chem. Soc.*, 1932, **54**, 4325.

By elimination of water between the hydroxyl groups of XII., XIII. and XIV., three dimethylxanthenes should be formed.

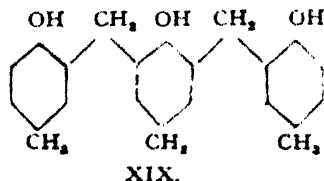
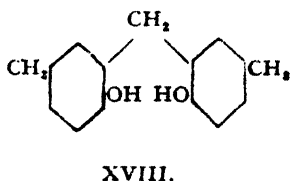


Pyrolysis of *m*-cresol resin has given a mixture of xanthenes, in which XV., m.p. 199°-200°¹⁵ has been identified, together with an unknown impure xanthene, m.p. 152°-154°, probably XVI. or XVII.

The phenols obtainable by pyrolysis should be *m*-cresol, *o*:3-, *o*:4- and *p*-xylenols, ψ -cumenol, *vic*- ψ -cumenol, *as*-hemellitenol and *iso*-durenol. It has been possible by fractional distillation of the phenols from (C) to isolate *o*:4-xynol, *p*-xynol and ψ -cumenol. The fact that no *o*:3-xynol was detected is considered as due to the method of separation of phenols, rather than to its absence, since the groupings contained in XVI. and XVII., one of which has been isolated, should yield this phenol on decomposition. The positive existence of both *o*- and *p*-linkages, shown by the phenols identified, implies high complexity of products in *m*-cresol resins.

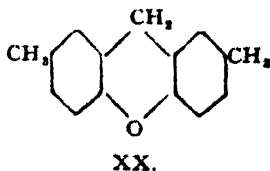
It cannot be inferred from the isolation of xanthenes from this and other pyrolytic processes, that these compounds exist as such in resins, but only that *o*-*o'*-dihydroxy groupings are present. No free xanthenes were ever detected in fraction (B), where they would distil if present in the free state.

p-Cresol, by virtue of its symmetry and possession of only two positions open to substitution, forms an extremely simple series of condensation products, there being only one possible isomeric for any given length of chain. The smallest possible chain compounds are XVIII. and XIX., both of which have previously been identified in resinous condensations.⁸ Both have now been isolated from the products of vacuum distillation, in agreement with Koebner's observations.



108 g. of *p*-cresol with 45 g. of formaldehyde yielded 33 g. of free *p*-cresol (A), 26 g. of (B), 21 g. of decomposition products (C) and 21 g. of residue (D).

The phenols theoretically derivable by pyrolysis are *p*-cresol, *m*-4-xynol and mesitol. None higher than *p*-cresol has been detected with certainty although higher boiling unidentified phenols have been noticed in small quantity. The neutral fraction has yielded 2 : 7-dimethylxanthene (XX)¹⁶ :



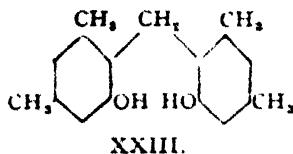
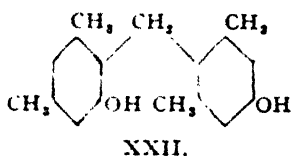
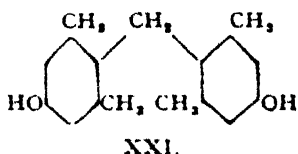
¹⁵ Gladstone and Tribe, *J.C.S.*, 1882, 41, 11.

¹⁶ M. R. Fosse, *C. rend.*, 1903, 136, 1006.

The supposition that xanthenes are formed during pyrolysis of resins by elimination of water between *o-o'*-hydroxy groups, is supported by an observation that simple heating of XVIII. is sufficient to remove water and to give a distillate consisting chiefly of XX. Furthermore, destructive distillation of the three-ring compound XIX., gave the same xanthene, together with phenolic material containing *p*-cresol. This latter experiment closely imitates the conditions existing during pyrolysis of resins.

Owing undoubtedly to its simple structure, Novolak from *p*-cresol exhibits a greater tendency to crystallisation than other phenolic resins. During previous work,⁶ in which condensations were carried out with para-formaldehyde in alcoholic solution, most phenols gave resinous solutions which merely became more viscous with time of condensation. The numerous isomerides formed, not necessarily of great length or of high melting-points, presumably formed a highly complex system soluble in alcohol, whereby precipitation of individual compounds was inhibited. During *p*-cresol experiments, a white substance was deposited, which increased considerably with time; it probably consisted of comparatively few long chain compounds of high melting-points, which were unable to form such a soluble system, and hence crystallisation occurred.

m-5-Xylenol resembles phenol in the number of condensation products it yields. The three possible dihydroxydixilylmethanes have all been isolated from resinous condensations.⁷ They have not been individually characterised with certainty, although there is some evidence that XXI. represents the compound of highest melting-point. All these compounds have now been identified in the products of vacuum distillation:



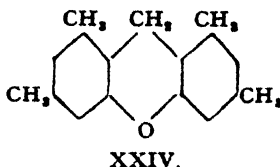
For the proportions of formaldehyde examined the variations in fractions (A), (B), (C) and (D) closely resembled those from other phenols.

The higher phenols anticipated by pyrolysis are *sym*-hemellitenol, *iso-ψ*-cumenol, durenol, prehnitenol, and pentamethylphenol. Of these there have been identified by fractional crystallisation *iso-ψ*-cumenol and durenol. The formation of these two substances shows that substitution has proceeded almost entirely in the *o*-positions, a surprising observation in view of the fact that, under alkaline conditions, *m*-5-xylenol gives a monoalcohol, which Auwers¹⁷ has shown to be *p*-hydroxyhemellityl alcohol. It is possible, however, that under acidic conditions *p*- and *o*-alcohols are formed together, that the *p*-alcohol immediately combines with xylenol to give XXI., and that the main condensation proceeds through the *o*-alcohol (*cf.* phenol condensation). Alternatively it is possible that the *o*-linkage is more easily ruptured by heat than the *p*-linkage.

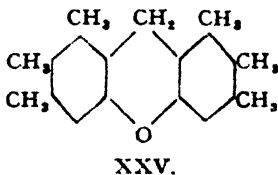
Steric hindrance effects probably oppose substitution of this xylenol in all three available positions, and therefore the tendency will be towards long chain compounds with little cross linking. Oil-solubility should thereby be favoured.

¹⁷ K. von Auwers, *Ann.*, 1906, 344, 271.

Only one xanthene would be expected from pyrolysis, 1:3:6:8-tetramethylxanthene XXIV, being derivable from the structure contained in XXIII.



This compound has been identified, crystallising from acetone in small glistening plates, m.p. 198°-200°. (Found: C 85.4 per cent.; H 7.85 per cent.; $C_{14}H_{18}O$ requires C 85.7 per cent., H 7.57 per cent.) At the same time a minute yield of a second material was isolated insoluble in caustic soda, which sublimes above 275°. It has been tentatively assigned the formula of a hexamethylxanthene (XXV.). The type of decomposition required to produce this compound has already been referred to under phenol, and there seems no reason to doubt its possibility in resins from other phenols.



Alkaline Condensations.—It is of interest that similar pyrolyses carried out with the products from alkaline phenolic condensations have yielded similar results. A commercial heat-hardening resin derived from *m*-cresol, on pyrolysis gave not only *m*-cresol, but higher homologues in which *o*-4-xylene has been detected. It is concluded that the basic structures of resins derived under acidic and alkaline conditions are closely related.

Although the results presented here assist elucidation of complex phenolic condensations, they yet leave numerous questions open to investigation. It is desirable, for example, not only to characterise the structure of the dihydroxydiarylmethanes produced, but to estimate their relative amounts, so that information will become available as to the extent to which particular isomerides influence physical properties of the resins. The isolation of polyring compounds from phenols other than *p*-cresol is a problem which may be solved by employing higher vacua during distillation of condensation products. There have been indications in the present work that fraction (B) from phenol condensations, contained constituents (less volatile than dihydroxydiphenylmethanes), which are suspected of being three ring compounds. Molecular weight determinations carried out on various resinous fractions obtained during working-up of the products would also be valuable in checking the degree of condensation achieved. Finally, a more complete examination of the products of pyrolysis, than that described above, is of evident importance.

The elucidation of these problems is a purely chemical concern. Assuming the nature of the compounds present in resins be ascertained in this way there still remains the more fundamental physico-chemical problem of determining the manner in which these substances co-exist to produce resins. In this field, valuable work has already been carried

out by von Weimarn, Tammann, Scheiber and others, whose concepts have been comprehensively discussed by Scheiber and Sändig.¹⁸

Summary.

1. Evidence supporting the hypothesis that Novolak resins consist of complex mixtures of chain compounds of phenol-methylene type is summarised.

2. This hypothesis is supported experimentally by :

(a) Isolation of condensation products of dihydroxydiarylmethane type, which are shown to decrease in yield with increase of formaldehyde.

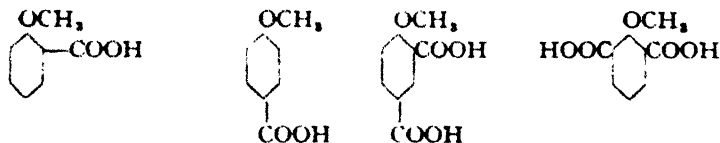
(b) Isolation of higher methyl homologues of phenols, and of xanthenes, by pyrolysis of resins.

In conclusion, the author thanks Professor G. T. Morgan, O.B.E., D.Sc., F.R.S., Director of Chemical Research, for permission to contribute this paper to the discussion.

*Chemical Research Laboratory,
Teddington, Middlesex.
July, 1935.*

GENERAL DISCUSSION.

Professor K. H. Meyer (*Genève*) said : Hemmi and I have made the following experiments. We interrupted the alkaline condensation of phenol and formaldehyde in concentrated solution by reaction with dimethyl sulphate to etherify the phenolic hydroxyl groups, and subsequently oxidised with permanganate to convert the lateral $-\text{CH}_2\text{OH}$ groups into carboxyl. We could isolate the following acids :

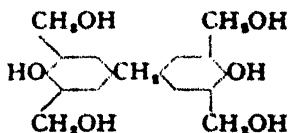


together with higher molecular compounds of the diphenylmethane series.

The acid $\text{CH}_3\text{O}-\text{C}_6\text{H}_3(\text{COOH})_2$ does not seem to be formed, which indicates

that under these conditions, either the velocity of the reaction of the di-alcohols with phenol is greater than the reactivity with formaldehyde, or else the trialcohol, when formed, reacts immediately with phenol.

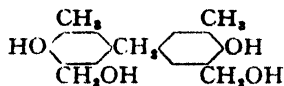
Dr. E. E. Walker (*Manchester*) said : Mr. Megson has dealt successfully with the condensation products formed under acid conditions and refers at the end of his paper to those formed under alkaline conditions. The simpler mononuclear phenol alcohols which can be isolated from alkaline reaction mixtures are well known, but some years ago a substance $\text{C}_{17}\text{H}_{16}\text{O}_6$ was isolated from such a reaction mixture in the laboratories of Imperial Chemical Industries Limited. This was found to be a derivative of 4 : 4'-dihydroxydiphenylmethane and almost certainly possesses the constitution :



¹⁸ J. Scheiber and K. Sändig, *Artificial Resins*, translated by E. Fyleman, London, 1931.

The manner in which a high molecular weight substance can be built up from this by condensation with free phenol and less highly substituted phenol alcohols is obvious.

Similarly it has been found that the constitution of the crystalline substance isolated from alkaline *o*-cresol formaldehyde condensation products is :



These observations seem to indicate that the first condensation takes place in the *para*-position.

If the matter is of sufficient interest it may be possible to publish details of the isolation of these substances and the evidence for their structure.

Mr. N. J. L. Megson (*Teddington*), in reply, said : Professor Meyer's results on the oxidation of methylated phenolic products confirm the *o-p*-substitution by formaldehyde in the phenolic nucleus. It is agreed that further condensation may proceed before addition of three methylol groups to the phenol nucleus, and it may be that a certain minimum length of chain is necessary before the tendency to condensation becomes less than that of addition, and cross-linking, with formation of infusible, insoluble products, becomes possible. Against this hypothesis is the report by Dr. Walker of the isolation of tetramethylol-*p-p'*-dihydroxydiphenylmethane, which implies probable branching of chains at an early stage. The certain identification of the compound would be of considerable interest, since substances of this type have hitherto only received unreliable description in patent literature. The compound is a methylol derivative related to the dimethyloldihydroxydiarylmethanes prepared by other workers from *o*-cresol, *p*-cresol and *m*-5-xynol.¹⁹

The orientation of derivatives of diarylmethanes presents difficulties, and despite statements by investigators working with them, there is surprisingly little direct evidence giving exact positions of substituents. Thus, unless Dr. Walker possesses information other than that provided by Granger,¹⁹ the constitution of the *o*-cresol-formaldehyde compound must remain speculative; it may be the 4:4', 2:4', or even 2:2'-dihydroxy-derivative of 3:3'-dimethyl-5:5'-dimethyloldiphenylmethane. The possibility of formation of three related isomerides together has already been reported for several phenols; few of them have been orientated. Hence publication by Dr. Walker of any results definitely justifying the belief that first condensation takes place in the *para*-position would clearly be of much value. The products obtained by pyrolysis of phenolic resins, which yield information on the relative positions of methylene and hydroxyl groups, have so far indicated that both *o*- and *p*-substitution occurs in *m*-cresol, but only *o*-substitution in *m*-5-xynol. More recent, unpublished, results have shown *o-p*-substitution in *o*-cresol.

There are grounds for Mr. R. H. Kienle's view that the structures contained in "Novolaks" may differ from those in hardening resins, but confirmation or otherwise of the belief cannot be obtained until the pyrolytic products from the resins have been examined in greater detail. The most that can be deduced is that certain groups, for example the phenol-methylene unit, appear to be common to both types of resin. Evidence from another type of experiment does, however, demonstrate the variations which may be caused by catalytic effects. During investigations on the production of phenolic resins from tar fractions with aqueous formaldehyde,²⁰ it was noticed that whereas pyridine readily caused

¹⁹ Granger, *Ind. Eng. Chem.*, 1932, **24**, 442; Koebner, *Z. angew. Chem.*, 1933 **46**, 251; Auwers, *Ber.*, 1907, **40**, 2537.

²⁰ Holmes and Megson, *J.S.C.I.*, 1933, **52**, 415T.

deposition of a lower layer of resin, ammonia, which is definitely a more rapid catalyst, only gave a resinous deposit after very prolonged condensation. In this case, solubility of resin in the tar neutral oil is apparently determined solely by the catalyst. This fact is best explained by assuming formation of two different structures as a result of catalytic action; possibly variations in oil-solubility are determined by differences in position of substitution of methylene linkages.

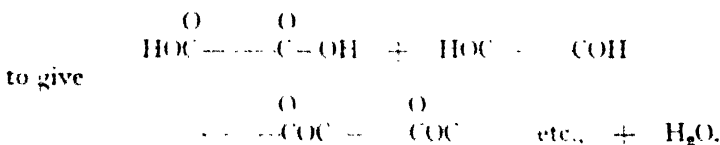
THE FORMATION OF HIGH POLYMERS BY CONDENSATION BETWEEN METALLIC POLYSULPHIDES AND DIHALOGENATED HYDROCARBONS AND ETHERS.

BY J. C. PATRICK.

Received 7th August, 1935.

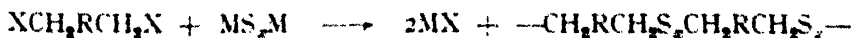
The general theory of formation of high molecular weight linear polymers by condensation between bi-functional compounds of low molecular weight to form products of large molecular mass has been so thoroughly reported in the literature that no extensive citation is believed to be advisable here.

A very thorough study of this type of reaction has been made by Carothers and his co-workers on the formation of polyesters, the reaction being of the general type:



One can, without taxing the imagination, conceive of the polymerisation of isoprene or butadiene as belonging to the same general type of phenomenon differing only in the fact that the reacting molecules are alike instead of different and that the "condensate" is one double bond per molecule. Therefore, no attempt will be made in this paper to distinguish between condensation and polymerisation.

When organic dihalides having CH_2X terminals, in which "X" denotes a halogen, are caused to react with metallic polysulphides, MS_xM , there usually results a linear polymer, of high molecular weight.



A few specific examples are as follows:

- (1) $\text{ClCH}_2\text{Cl} + \text{M}_2\text{S}_2 \rightarrow \text{---CH}_2\text{S}_2\text{CH}_2\text{S}_2\text{CH}_2\text{S}_2\text{---}$
- (2) $\text{Cl}(\text{CH}_2)_3\text{Cl} + \text{M}_2\text{S}_2 \rightarrow \text{---}(\text{CH}_2)_3\text{S}_2(\text{CH}_2)_3\text{S}_2(\text{CH}_2)_3\text{S}_2\text{---}$
- (3) $\text{Cl}(\text{CH}_2)_6\text{Cl} + \text{M}_2\text{S}_2 \rightarrow \text{---}(\text{CH}_2)_6\text{S}_2(\text{CH}_2)_6\text{S}_2(\text{CH}_2)_6\text{S}_2\text{---}$
- (4) $\text{ClC}_2\text{H}_4\text{OC}_2\text{H}_4\text{Cl} + \text{M}_2\text{S}_2 \rightarrow \text{---C}_2\text{H}_4\text{OC}_2\text{H}_4\text{S}_2\text{C}_2\text{H}_4\text{OC}_2\text{H}_4\text{S}_2\text{---}$
- (5) $\text{ClC}_2\text{H}_4\text{OC}_2\text{H}_4\text{OC}_2\text{H}_4\text{Cl} + \text{M}_2\text{S}_2 \rightarrow \text{---C}_2\text{H}_4\text{OC}_2\text{H}_4\text{OC}_2\text{H}_4\text{S}_2\text{C}_2\text{H}_4\text{OC}_2\text{H}_4\text{OC}_2\text{H}_4\text{S}_2\text{---}$

Many of the linear polymers of the type given above that have been studied either have, or can be readily made to assume, highly rubber-like characteristics.

It will be noted that in the five examples given, Nos. 1, 2 and 3 involve the reaction of a simple hydrocarbon dihalide, whereas Nos. 4 and 5 show the reaction with a hydrocarbon chain containing ether linkages.

Since symmetrical dichloroethane, or ethylene dichloride may be considered typical of the first type of organic reactant, *i.e.*, the simple hydrocarbon dihalide, its reactions will be given in some detail.

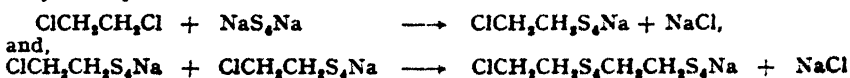
If the polysulphide chosen is a solution of sodium polysulphide properly prepared and having the empirical formula Na_2S_4 , it will react very readily with its equivalent weight of ethylene dichloride in the presence of a dispersing agent such as magnesium hydroxide to form a somewhat latex-like suspension of the polymer. When the suspension of particles has been washed free from the by-products of the reaction by repeated settling and decantation with water, it will coagulate to an elastic rubbery mass on acidification of the liquid.

This polymer is unique in that it shows a degree of extensibility and retractability comparable with natural rubber and also exhibits the Joule effect. According to unpublished observations of Dr. J. R. Katz, films of the polymer exhibit an X-ray fibre diagram on stretch comparable with that given by rubber under similar conditions.

Another peculiar analogy with rubber is noted when the polymer is mixed with, for example, zinc oxide and heated. At temperatures customarily used in the vulcanisation of rubber, a phenomenon superficially strikingly similar to vulcanisation takes place. The originally, somewhat plastic mix becomes firm and strongly elastic, and the effect is even more marked if a pigment of the type of carbon black, which exerts such a strongly reinforcing effect on rubber, is present.

Certain suggestions regarding the chemical structure of the ethylene polysulphide polymers will be advanced.

The reaction between ethylene dichloride and sodium tetrasulphide may be represented as:



and this process may continue as each new unit is itself bifunctional and capable of reaction at one end or the other, either with a similar unit or with either of the original reactants which happens to be in excess until either, or both, of the primary reactants is exhausted after which reaction with chain growth may continue between the already formed units with, however, rapidly diminishing frequency as the average mass of the units increases.

According to the above hypothesis the polymer would not have chlorine terminals if the polysulphide were kept always in excess, and the empirical formula of the large molecule would approach very nearly to $\text{C}_2\text{H}_4\text{S}_4$. This is confirmed by experimental data.

This hypothesis also postulates high molecular weight and this is also indirectly confirmed by experiment, because, while it has not been possible to determine the average molecular weight of the polymer, all attempts to determine this value have indicated that it is large.

Since there is no good reason to suppose any alteration in the structural relationships of the hydrocarbon residue in this reaction it will be assumed that the integrity of the $-\text{CH}_2\text{CH}_2-$ radical is maintained. The arrangement of the S_4 complex admits of several hypothetical groupings. One might postulate the polysulphide group as

extended into a four-sulphur chain in which each sulphur atom is linked to its neighbour or to a carbon atom by a covalent linkage such as $-\text{C}:\text{S}:\text{S}:\text{S}:\text{S}:\text{C}-$, in which each sulphur atom is of equal value as a link in the chain. Another equally valid hypothesis is to assume

S S

a configuration for the polysulphide group such as $-\text{C}:\text{S}:\text{S}:\text{C}-$, in which two only of the sulphur atoms are essential to the integrity of the chain and two others, possibly co-ordinately linked to the sulphur atoms in the chain might be regarded as likely to considerably modify the physical properties of the molecule. This assumed structure would lead one to suspect that the two co-ordinately linked sulphur atoms would be more easily removed than the two sulphurs each covalently linked to carbon, and that their removal, while modifying more or less extensively the properties of the molecule, would not necessarily disturb the fundamental integrity of the chain.

Experimental data show conclusively that in the molecule of $\text{C}_2\text{H}_4\text{S}_4$, two of the sulphur atoms are combined in a very different manner from the other two. For example, if a suspension containing one empirical molar weight of the ethylene tetrasulphide polymer is treated with a solution containing 1.2 mols of sodium hydroxide, and is heated to 80° or 90° C. with agitation for about an hour, the red polysulphide solution of the metal is formed, and when the white somewhat granular residue is washed and dried its analysis always approaches very closely to the empirical formula $\text{C}_2\text{H}_4\text{S}_2$. If now the disulphide derivative is again subjected to the same treatment with a fresh solution of sodium hydroxide, the polysulphide of the metal, if formed at all, will be present only in minute quantity, and when the organic derivative is removed and analysed its empirical formula is substantially unchanged.

That the tetrasulphide derivative might have consisted originally of a solid solution of two gram atoms of elementary sulphur in one mol of $\text{C}_2\text{H}_4\text{S}_2$ is disposed of by the fact that extraction with such solvents as boiling acetone does not remove free sulphur and, even more conclusively, by sublimation of the tetrasulphide in a "molecular still" under high vacuum, in which case the empirical formula and physical properties of the sublimate correspond to $\text{C}_2\text{H}_4\text{S}_4$.

As might have been expected, the physical properties of the substance have undergone a change due to the removal of two sulphur atoms from the molecule.

The pale yellow tetrasulphide derivative is elastic and quite rubbery whereas after removal of the two sulphur atoms from the molecule the disulphide is a somewhat harsh granular powder, usually white in colour. This powder does not have a definite melting-point. It usually begins to soften perceptibly at around 130° C. and has become a viscous amber-coloured liquid at about 180° C., above which temperature evidences of incipient decomposition are observed. That the molecular weight is large is indicated by the fact that the polymer is practically unaffected by any organic solvent. It is not even swollen by carbon disulphide.

In view of the fact that the removal of two sulphur atoms from each unit of $\text{C}_2\text{H}_4\text{S}_4$ caused a transition in physical properties from a rubbery elastic substance to a granular thermoplastic powder, two interesting questions present themselves. Can the two sulphur atoms be replaced with resumption of all the original rubber-like qualities?

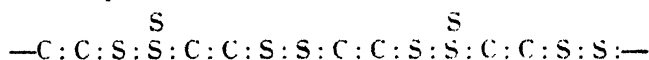
Would considerably less than two gram atoms of sulphur per empirical molar weight of $C_2H_4S_2$ suffice to impart rubbery characteristics?

The experimental evidence gives a complete affirmative to both questions.

If one empirical mol of $C_2H_4S_2$ is intimately mixed with two gram atoms of sulphur especially in the presence of one or two tenths of a per cent. of an accelerator of the alkaline type (diphenyl guanidine is very suitable), and heated for twenty-four hours in an oven at 120° to 130° C. the sulphur recombines and a soft elastic mass is obtained. The same result is produced even more completely if the sulphur and the disulphide derivative are mixed on the rolls of a laboratory rubber mill with, in addition to the accelerator, about 5 per cent. by weight of zinc oxide. In this case the mass becomes plastic almost at once but will stiffen to a hard board-like consistency when cold. If now the mix is subjected to a temperature of 145° C. for about thirty minutes, an elastic tough substance resembling cured rubber is obtained. Here also attempts to remove sulphur by the use of selective solvents are not successful.

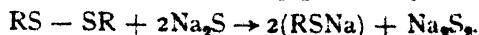
The answer to the second question as regards the minimum amount of sulphur competent to develop permanently rubber-like properties is easily determined by the last procedure mentioned above. When the disulphide derivative is mixed on the mill rolls with varying proportions of sulphur and the resulting mixes heated as described, it is found that sulphur in the proportion of about one gram atom to two empirical molar weights of the disulphide derivative, that is, an amount of additional sulphur which would give an empirical formula of $C_2H_4S_{2.5}$, suffices to confer permanent rubberiness to the full extent, but that lesser amounts of sulphur are not sufficient.

According to the hypothesis made above concerning the co-ordinate combination of sulphur, this amount of sulphur would roughly correspond to about one co-ordinately combined sulphur atom to each two units of the carbon-sulphur chain:



It is interesting to note that the addition of sulphur to form a rubbery elastic substance does not take place under the conditions described above if only one sulphur atom is present in a unit of the chain. For example, polymeric ethylene sulphide, $-CH_2CH_2SCH_2CH_2S-$, does not exhibit this phenomenon.

Attempts to remove more sulphur from the polymeric ethylene disulphide have been unsuccessful without complete decomposition of the molecule. However, in the presence of a suitable reducing agent the S—S bond can be broken. If one empirical molar weight of $C_2H_4S_2$ in suspension in water is first "stripped" of two sulphur atoms with sodium hydroxide solution and, after removal of the polysulphide formed, the mol of $C_2H_4S_2$ remaining is heated with two mols of Na_2S , in solution, to about 90° C. with suitable agitation for several hours, a completely water-soluble product is obtained. A reddish solution of sodium polysulphide is also formed which is found on analysis to correspond to the empirical formula Na_2S_3 . Perhaps:

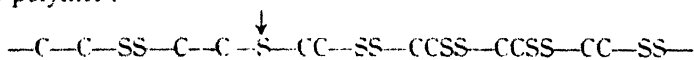


When acidified the aqueous solution obtained by reduction of the ethylene disulphide evolves hydrogen sulphide and eliminates sulphur due to the decomposition of the sodium disulphide. On complete

acidification it also eliminates an oily substance and on steam distillation a fair amount of ethylene mercaptan is obtained. If now one mol of this mercaptan is treated with the calculated amount of sodium hydroxide solution to form the di-mercaptide and the solution of sodium ethylene di-mercaptide is then treated with an oxidising agent such as a sodium tetrasulphide solution or a hypohalite, a substance having most of the chemical and physical properties of the ethylene disulphide polymer, from which the mercaptan was derived, is obtained.

If, instead of acidifying the mercaptide solution, obtained by reduction of $C_2H_4S_2$ with sodium sulphide, the aqueous alkaline solution is filtered and oxidised at boiling temperature by passage of a current of air the identical parent substance is obtained, and when this polymer is treated with additional sulphur in the manner described above the elastic rubbery properties are developed in their entirety.

It is believed that the slight differences noted between the product obtained by oxidation of a pure sodium ethylene di-mercaptide, and that derived from the oxidation of the mercaptide solution obtained by first "stripping" then reducing the derivative of ethylene tetrasulphide without prior separation of the mercaptan by distillation, is due to the presence of a certain amount of sodium monosulphide in the parent polysulphide. This on reaction with $C_2H_4Cl_2$ would lead to the formation of a certain proportion of thio-ether linkages in the molecule of the polymer:

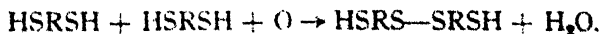


The chain on reduction may be expected to split only between the $-S-S-$ linkages with the result that the mercaptide solution should contain in addition to $NaSCH_2CH_2SNa$ also a certain amount of the sodium salt of dimercapto-thioether $NaS-C-C-S-C-C-SNa$.

The fact that the rubbery tetrasulphide polymer can be reduced to the disulphide polymer, that this can in turn be reduced to a mixture of mercaptans of fairly well established structure which then by oxidation regenerates the polymeric disulphide, and that the disulphide then can undergo further oxidation with free sulphur to a polymeric tetrasulphide substantially identical with the original polymer, would seem to justify the following inferences:

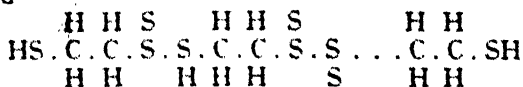
That the fundamental recurring unit in the chain is $-CH_2CH_2SS-$ with an occasional thioether linkage $-CH_2CH_2SCH_2CH_2-$.

That the terminal or end groups after acid coagulation are sulphhydryl groups $-SH$ the same as those of the low molecular weight mercaptans from which the disulphide polymer can be synthesised by oxidation,



That the polysulphide polymers of higher sulphur rank than the disulphide polymer are co-ordination compounds with sulphur.

A tentative formula for the rubbery tetrasulphide polymer can now be constructed



The experimental data prove quite conclusively that the permanent extension-retraction elasticity, *i.e.*, rubberiness, of the ethylene derivative is dependent upon the presence of not less than a definite minimum

excess of sulphur over that required by the empirical formula $C_2H_4S_2$. This excess sulphur is believed to be co-ordinately combined.

As representative of the dihalides having ether linkages one may select β - β' dichloroethyl ether for discussion.

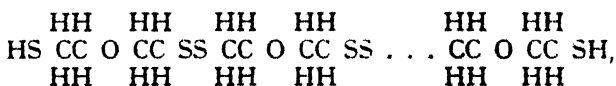
When this dichloroethyl ether is reacted with sodium tetrasulphide under similar conditions to those described under ethylene dichloride, a coagulable suspension of the polymer is obtained.

This product shows the analogies with rubber to an even greater degree than is the case with the ethylene derivative.

When the same methods of investigation are applied to the polymeric ether tetrasulphide as were described in the case of the ethylene tetrasulphide, a very close parallelism can be demonstrated. There is, however, one rather remarkable difference. When the ether tetrasulphide polymer is treated with sodium hydroxide solution until no further sulphur can be removed, the latex-like suspension remaining will coagulate into a white highly elastic mass when treated with acid. This elastic polymer has by analysis the empirical formula $OC_4H_8S_2$. When dried and sheeted out it closely resembles natural rubber in its "liveness." This polymer undergoes a typical vulcanisation when compounded with zinc oxide or litharge and, when properly compounded with reinforcing pigment and cured, it develops a degree of elasticity and resistance to tear fully equal to rubber.

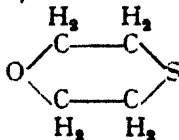
This ether disulphide polymer can be made to take up two gram-atoms of sulphur per mol of $OC_4H_8S_2$ to reform the tetrasulphide polymer, but the addition of sulphur does not in this case enhance the rubber-like properties. The same observation applies in the case of the polymeric disulphide derivative of chloroethoxy chloroether.

The ether disulphide polymer on treatment with sodium sulphide is reduced to mercaptide from which the polymer can be regenerated by oxidation. Therefore, similar inferences regarding its structure will be made as were made in the case of the ethylene derivative.



which in the large molecule approaches closely the ratio required by the empirical formula $OC_4H_8S_2$ given by analysis.

It is of interest that in the reaction between polysulphide solutions and β - β' dichloroether about 15 to 20 per cent. of the dichloroether, depending on the type of polysulphide solution used, goes to form the cyclic compound 1.4 thioxane,



The thioxane formation is believed to be accounted for by the presence of monosulphide in the polysulphide solution, since a high yield of thioxane is obtained when β - β' dichloroether is reacted with pure sodium monosulphide solutions. In this reaction only a small yield of the chain polymer,

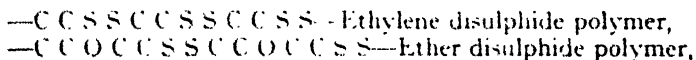


is obtained as a somewhat granular white powder giving no evidence of elasticity whatsoever.

At this point it may be well to compare probable chemical structure of the unit of the polymers with gross physical properties in tabular form.

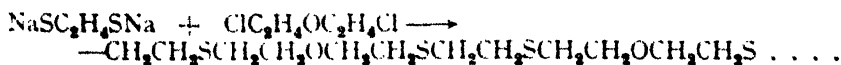
Unit of Polymer =	Approximate Physical State.
$-\text{CH}_2\text{S}$	Powder
$-\text{CH}_2\text{SS}$	Powder
$-\text{CH}_2\text{SS}-$ SS	Rubber-like
$-\text{CH}_2\text{CH}_2\text{S}-$	Powder
$-\text{CH}_2\text{CH}_2\text{SS}-$	Powder
$-\text{CH}_2\text{CH}_2\text{SS}-$ SS	Rubber-like
$-\text{CH}_2\text{CH}_2\text{CH}_2\text{S}-$	Powder
$-\text{CH}_2\text{CH}_2\text{CH}_2\text{SS}-$	Powder
$-\text{CH}_2\text{CH}_2\text{CH}_2\text{SS}$ SS	Rubber-like
$-\text{C}_2\text{H}_4\text{OC}_2\text{H}_4\text{S}-$	Powder
$-\text{C}_2\text{H}_4\text{OC}_2\text{H}_4\text{S S}-$	Rubber-like
$-\text{C}_2\text{H}_4\text{OC}_2\text{H}_4\text{S S}-$ S S	Rubber-like
$-\text{C}_2\text{H}_4\text{OC}_2\text{H}_4\text{OC}_2\text{H}_4\text{S}-$	Powder
$-\text{C}_2\text{H}_4\text{OC}_2\text{H}_4\text{OC}_2\text{H}_4\text{S S}-$	Rubber-like
$-\text{C}_2\text{H}_4\text{OC}_2\text{H}_4\text{OC}_2\text{H}_4\text{S S}-$ S S	Rubber-like.

In view of the fact that whereas no rubber-like characteristics were exhibited by the ethylene disulphide polymer, but were developed when oxygen was present linked to the beta carbon atom as in the disulphide derivative of β - β' dichloroether,



investigations are now in progress to determine whether or not the monosulphide derivatives can by any structural rearrangement be made to assume the typical rubber-like properties.

For example, by reacting sodium ethylene dimercaptide with dichloroether an interesting variation in the sequential arrangement can be made :



This polymer does not, however, exhibit rubber-like properties.

In consideration of the fact that one of the most remarkable properties displayed by several of the polysulphide polymers is their capacity to undergo a change at least superficially analogous to the vulcanisation of the diene polymers, a few comments on this phenomenon will be made.

As investigations are now in progress which it is hoped will clear up some of the more obscure points on the subject of cure or vulcanisation, no extended discussion would be justified.

The heat cure phenomena exhibited by the polysulphide polymers appear to involve in every case an oxidation process. Oxidising agents such as di- and tri-nitro benzene, benzoyl peroxide, etc., promote the cure, whereas reducing agents such as for example pyrogallol and zinc dust greatly retard and in many cases inhibit the curing process.

A number of metallic oxides are very effective in promoting cure, among which zinc oxide and cupric oxide are perhaps to be preferred. It should be noted also that a trace of moisture in the mix promotes the curing process.

For example, if the ether disulphide polymer is placed in a mould in a curing press, the platens of which are heated to 145° C. and the mould is exposed to this temperature for thirty minutes, then cooled and removed, no particular change is observed, except that the material is usually somewhat more plastic than before heating. If the time of exposure to the temperature is increased, a tendency to stickiness of the surfaces of the sample becomes noticeable. If, however, before subjecting to the curing temperature, 100 parts by weight of the plastic polymer are intimately mixed, or compounded, with 10 parts by weight of powdered zinc oxide and heated as described, a very different result is obtained. The rather plastic mass has taken the exact shape of the mould, and has developed toughness and "nerve." When a strip of the material is pulled out to an elongation of about 500 per cent. of its original length, the piece becomes warm and, when permitted to resume its former length, a perceptible cooling effect is noted. If stressed beyond its strength it breaks with a sharp snap.

If the time of exposure to temperature is doubled, the toughness of the material is found to have increased. The ultimate elongation at break has decreased, but the stress required to produce any given deformation (the modulus) has increased. When, in addition to the zinc oxide, about 20 parts by weight of carbon black is compounded with the polymer, all of the physical properties are markedly enhanced.

To show graphically the very marked change in physical properties, and presumably in internal structure, brought about by heating the polymer in the presence of suitable curing agents, a stress-strain diagram is presented. In this diagram, the loads required to cause a given elongation of the test specimen are plotted against the percentage of the original length represented by that elongation. For convenience points were chosen at 100 per cent. elongation and at multiples of 100 per cent. and a smooth curve drawn through the points so established. A low tensile soft stock was chosen, as such a compound shows most clearly the change in shape and the displacement of the curve with increasing time and/or temperature.

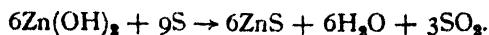
It is of interest to compare the general shape of these curves with the stress-strain diagram deduced on theoretical grounds for rubber by Mack.

The statement was made that the phenomena of cure displayed by the polysulphide polymers appear to be caused or accompanied by an oxidation process. Zinc oxide is not, however, ordinarily regarded as an oxidation agent.

Investigation has shown that when any of the vulcanisable polysulphide polymers is cured with zinc oxide, or zinc hydroxide since traces of moisture are invariably present and have in some cases been demonstrated to be essential, a certain amount of zinc sulphide is always present after cure. The exact proportion of zinc oxide changing to the sulphide during cure has not been determined with a sufficient degree of accuracy, on account of the very considerable experimental difficulties attending its quantitative separation from the vulcanised mass.

Obviously then, a certain amount of hydroxyl has been replaced by sulphur in combination with the zinc. When zinc hydroxide combines with sulphur a considerable potentiality for oxidation is displayed.

For example, when powdered zinc hydroxide is intimately mixed with powdered sulphur and the mixture is heated in a tube, a considerable amount of sulphur dioxide is evolved. The complete reaction may be represented as:



As it has been shown above in commenting on the hypothetical structure of the linear polysulphide polymers, the presence of terminal

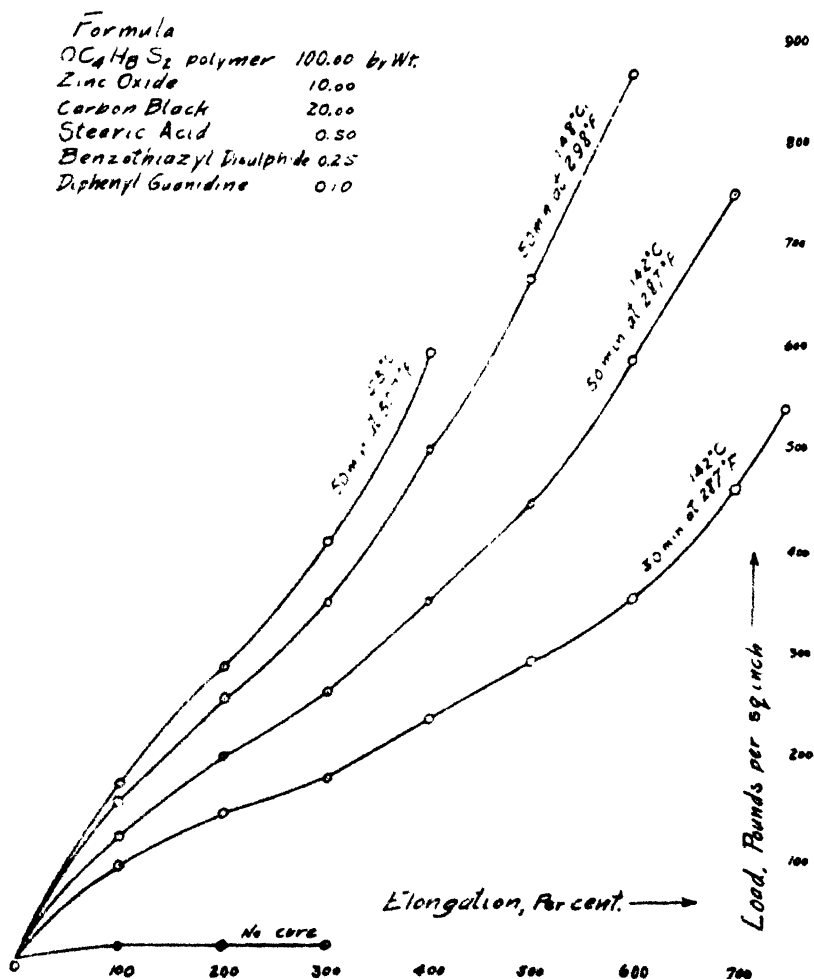
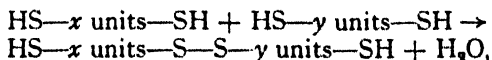


FIG. 1.

—SH groups is a very plausible inference from their synthesis from the mercaptans. In a way the polymers may themselves be considered, according to this hypothesis, to be mercaptans of very high molecular weight.

Considered in this way, if it is shown that "vulcanisation" of these polymers always involves an oxidation, the thought immediately suggests itself that at the elevated temperatures used a further oxidation polymerisation takes place and that the "heat cure" of these polymers

involves only the raising of the average length of the chain to a higher level. In other words, two chains, one x units in length, and the other y units long, both having —SH end groups may undergo mutual oxidation if a terminal group of one happens to be in juxtaposition with a terminal group of the other to give,



the two original chains having coalesced through an —S—S— linkage to give a similar chain $x + y$ units long.

This simple hypothesis would "explain" all the phenomena of heat vulcanisation as due to increase in the average molecular weight or increased degree of polymerisation. While it is probable that this hypothesis would account for a part and perhaps a large part of the phenomena of heat vulcanisation of the polysulphide polymers, it is also probable that other factors than linear polymerisation may play a part. For example, the marked increase in resistance to solvent penetration with increased cure would strongly suggest the possibility of cross linkages taking place with a "tying in" of the whole structure.

In the present state of the investigation, no mechanism by which this cross linking might take place can be suggested.

Aside from their scientific interest, several of the elastic polysulphide polymers have furnished the technologist with very valuable tools, because although they strongly resemble rubber in elasticity, capability of reinforcement and modification by pigments, and especially in their ability to undergo "cure" by heat in which they pass from a fairly plastic workable mass to a tough elastic final form; they differ uniquely from rubber and its cognate polymers in their chemical stability and their resistance to attack by organic solvents and by oxidation.

Certain of these polymers when properly compounded and cured are adaptable for use over a very wide temperature range. For example, compounds have been made which were as flexible at 50°F. below zero as at ordinary temperatures, and the same compound underwent no appreciable change when immersed in hot lubricating oil for days at 212°F.

In view of the several hypotheses advanced in recent years to account for the extension-retraction elasticity of rubber, it would be of great interest to properly evaluate the significance of the peculiar analogies in physical behaviour of many of the polysulphide polymers when compared with the characteristic properties of rubber, because in spite of the obviously very different chemical constitution of the polysulphide polymers, it appears probable that the parallels are so numerous as to rule coincidence out of court, and that a more plausible assumption under the circumstances is that some fundamental structural similarity and spatial relationship obtains.

On the other hand, the very differences in chemical constitution of the rubber-like polysulphide polymers as compared with that of rubber and other diene polymers may be of service by shedding an oblique light on the subject of what is necessary in the way of chemical structure and space relationships to cause a molecule to be rubber-like.

Summary.

A description has been given of certain highly rubber-like linear polymers derived from dihalogenated hydrocarbons and dihalogenated ethers when these compounds are reacted with polysulphides.

A theory of chemical structure has been suggested based on the oxidation-reduction phenomena exhibited by these polymers.

A partial theory of the mechanism of the heat vulcanization of these polysulphide polymers has been advanced.

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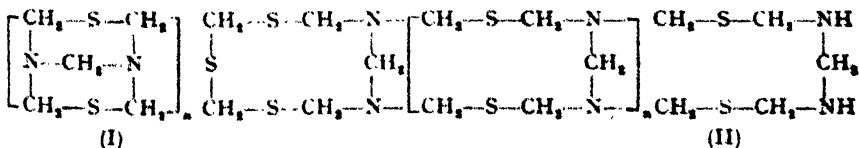
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I wish to acknowledge my indebtedness to the valuable assistance given by Dr. S. Maner Martin, Jr., of the Thiokol Corporation Research Laboratory in carrying out the experimental work to which reference has been made in this paper.

GENERAL DISCUSSION.

Dr. R. J. W. Le Fèvre (London) said: The reaction between methylene dichloride and alkali sulphide solutions having been expressed generally as $\text{Cl} \cdot \text{CH}_2 \cdot \text{Cl} + \text{M}_2\text{S}_x = -\text{CH}_2\text{S}_x \cdot \text{CH}_2\text{S}_x \cdot \text{CH}_2\text{S}_x$ —it becomes of interest to remark that an entirely different course is followed when M is NH_4 from that when it is Na or K. In collaboration with Mrs. C. G. Le Fèvre, an examination was made some years ago^{1, 2} of the reaction between aqueous formaldehyde (by hydrolysis equivalent to CH_2Cl_2) and solutions of ammonium sulphide or polysulphide. When these reagents were mixed, a white precipitate was formed after a definite period of induction which depended in a regular manner on the concentrations of the reactants and the temperature.³ From analysis and various reactions of the substance, detailed in the references^{1, 2, 3}, the conclusion was reached that it was a highly polymerised compound built up of units, shown in (I), associated together in much the same way as Hess⁴ at one time supposed the glucose anhydride units to be in cellulose.

However, all the known facts are just as completely represented by the structure (II), which is now proposed. This has the advantage that it allows the gradual growth of macro-molecules to be formulated throughout by the accepted mechanisms (aldol additions and water eliminations) of current organic chemistry. The recorded physical properties, especially the solubility, suggests that n is a large number. This agrees with the analytical data^{1, 2}, which corresponded with an empirical formula $(\text{CH}_2)_n\text{N}_2\text{S}_2$ (I), inasmuch as a considerable number of the intermediate



¹ Le Fèvre and Le Fèvre, *J.C.S.*, 1932, 1142.

² *Ibid.*, 1932, 2087.

³ Le Fèvre and Macleod, *J.C.S.*, 1931, 474.

⁴ Hess, *et alia*, *Annalen*, 1923, **435**, 1.

(CH_3)₃N₂S₂ units have to be inserted between the head and tail groups of (II) before the percentage of sulphur is lowered and that of nitrogen is raised to the order of that found experimentally for each of these elements ; the variability of analyses with the manner of preparation (3) is also directly explicable on a basis of (II), since n should be expected to be affected by concentration of reactants, the temperature of reaction, etc.

THE CONSTITUTION OF HYDROUS OXIDE GELS AND SOLS.

BY HARRY B. WEISER and W. O. MILLIGAN.

Received 10th July, 1935.

Hydrous Oxide Gels.

Hydrous oxide is the general term applied to gelatinous precipitates thrown down from salt solutions when the p_{H} is above a certain value which varies with different salts. The term as we have used it for more than a score of years implies that gel water is retained by the colloidal particles as a result of adsorption and capillary forces ; hence the water content of a given hydrous oxide is purely accidental depending on the exact method of formation and drying, the temperature, and the age of the sample. A hydrous oxide differs from a hydrated oxide in that the water in the latter is chemically combined in definite stoichiometric proportions. Some hydrated oxides like $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ and $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ give gelatinous precipitates which contain varying amounts of adsorbed water depending on the conditions of precipitation. Such preparations are designated as hydrous hydrated oxides. By the application of X-ray analytical methods, it has been established in a number of cases that hydroxyl groups are present. Gelatinous precipitates of such compounds are called hydrous hydroxides. On standing, the primary colloidal particles of the hydrous oxides and hydroxides grow and lose water spontaneously, causing the mass to assume a less gelatinous and more granular character. This spontaneous transformation from a loose voluminous precipitate to a granular mass is accompanied by a decrease in the solubility, the adsorbability, and the peptizability of the compounds.

The view that the hydrous oxide gels consist of colloidal particles of oxide or of a simple hydrate with adsorbed and entrained water was defended by van Bemelen¹ almost a half-century ago. This rather elementary concept of the constitution of the oxide gels is not accepted by certain investigators in this field. To illustrate the divergent views, a few typical oxide gels will be considered.

The Brown Gel of Ferric Oxide.

Dehydration Isobars.—The dehydration isobars for the brown gel of ferric oxide, commonly prepared by adding a base to a solution of a ferric salt, are smooth curves showing no evidence of the presence of hydrates. Typical of such adsorption isobars are the curves of Simon and Schmidt² which are reproduced in Fig. 1. Curve I is for a relatively

¹ *Rec. trav. chim.*, 1888, 7, 106 ; *Die Absorption*, 1910.

² *Kolloid-Z. (Zsigmondy Festschrift)*, 1925, 36, 65.

coarse sample formed by precipitation from a ferric nitrate solution with ammonia, and Curve 2 is for a finer grained sample thrown down from a cold ferric chloride solution with ammonia.

Although the dehydration isobars for the brown gel indicate the absence of hydrates, there is a difference of opinion as to how the water is held. Hüttig³ suggests that the water in hydrous oxides which give curves like those in Fig. 1, is "osmotically bound" water rather than water held in capillaries or adsorbed on the surface of the solid phase. This concept of osmotically bound water originated as a result of the observation that a number of the hydrous oxides give dehydration isobars like those in Fig. 1 which can be represented by an equation similar to van't Hoff's osmotic pressure law. Assuming that the osmotic pressure follows the gas laws, the van't Hoff equation takes the form

$$\ln \frac{p_0}{p} = \frac{n_1}{n},$$

in which p_0 is the vapour pressure of pure water; p , the vapour pressure of the solution at the same temperature; n_1 , the number of dissolved molecules; and n , the number of molecules of the solvent.

For oxide-water systems which give dehydration curves like those in Fig. 1, the value of n_1 might be set equal to 1 since the amount of the dry solid phase is constant. It was found, however, that in order to make the equation fit, it was necessary to multiply the constant number of molecules of dry solid ($n_1 = 1$) by an association or dissociation factor, k . The osmotic law equation thus takes the form

$$\log \frac{p_0}{p} = \frac{k}{n},$$

where p_0 is the vapour pressure of pure water which is a function of the temperature; p , the constant vapour pressure at which the dehydration is carried out; n , the water content of the solid phase; and k , a constant. Applying this equation, the value of k has been found to be constant and equal to approximately 4 for the dehydration of hydrous zirconia and of hydrous thorium; 2, for hydrous titania; 3, for certain hydrous ferric oxides; 1, for hydrous lead peroxide; 3 or 7, for white hydrous tungstic oxide, etc. On the basis of these observations it was assumed that the water is osmotically bound by the solid phase. This means that oxide-water systems which obey the modified osmotic law are in reality solid

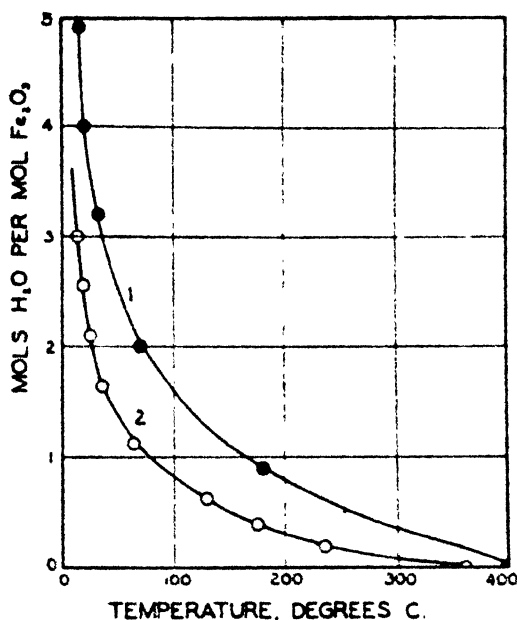


FIG. 1.—Dehydration isobars for hydrous ferric oxide.

³ *Fortschr. Chem., Physik, physik. Chem.*, 1924, 18, 5; *Kolloid-Z.*, 1932, 58, 44.

solutions in which the water is free to move about in the solid phase. Hydrrous oxide gels like alumina, chromic oxide, certain samples of ferric oxide, etc., which give dehydration isobars that do not obey the modified osmotic equation, are assumed to be mixed types in which only a part of the water is osmotically bound, the remainder being held in capillaries or adsorbed on the surface of the solid. Similarly, a definite crystalline hydrate like yellow tungstic oxide monohydrate which gives a dehydration isobar without sharply defined steps, is assumed to be a mixed type in which a part of the hydrate water is chemically bound in the orthodox sense and a part is free to move throughout the crystal lattice of the solid phase.

Although Hüttig has shown that the dehydration isobar of certain hydrrous oxides may be represented approximately by a modified form of the osmotic equation, it does not follow that in such cases the water is in solid solution in the oxide. In the first place, one would expect to get the same general type of curve for the gradual loss of adsorbed water with rising temperature. Indeed, the dehydration isobars for hydrrous ferric oxide, hydrrous zirconia, etc., may be represented by an adsorption equation of the Freundlich type.⁴ Moreover, many typical hydrrous oxides give curves which may be represented by the adsorption equation and which do not fit the modified osmotic equation. It does not follow necessarily in either case, that conformity of results with the equation is proof of the correctness of the assumptions on which the equation is based.

Dehydration Isotherms.—The dehydration isotherms of the brown gel are in general smooth curves which give no indication of hydrate formation; but Thiessen and Köppen⁵ obtained isotherms with breaks indicating the formation of 8 to 10 different hydrates during the dehydration of a ferric oxide gel resulting from the hydrolysis of ferric ethylate. The experiments of Thiessen and Köppen have been repeated⁶ and extended under very carefully controlled conditions which allowed ample time for equilibrium conditions to be set up. A typical set of isotherms which show no indication of breaks is reproduced in Fig. 2.

Foote and Saxton⁷ attempted to determine the manner in which water was held, by observing the volume changes on freezing the precipitated oxide. They came to the conclusion that the water which freezes gradually with falling temperature is held in capillaries, whereas water which cannot be frozen is in the "combined" or "bound" state. The "combined" water is given up slowly on heating the precipitate with water, with no tendency toward simple ratios between ferric oxide and water; and when once dehydrated, the material does not take up water to form hydrates. It was assumed, therefore, that the ferric oxide and water "combine" in indefinite proportions, which is essentially a case of solid solution rather than of adsorption. It is now known that the failure of gel water to freeze at a certain temperature is no criterion for determining whether water is dissolved or adsorbed.⁸

Willstätter and co-workers⁹ claim that the water in the gel is held in part as chemically combined hydrate water and in part as adsorbed

⁴ *Kolloidchemie*, 1930.

⁵ *Z. anorg. Chem.*, 1930, 189, 113.

⁶ Weiser and Milligan: *J. Physic. Chem.*, 1935, 39, 25.

⁷ *J. Am. Chem. Soc.*, 1916, 38, 599; 1917, 39, 1108.

⁸ Cf. Jones and Gortner: *J. Physic. Chem.*, 1932, 36, 424 et seq.; Kistler, *Reported at Meeting of the American Chemical Society*, April, 1935.

⁹ *Ber.*, 1924, 57B, 1082.



PLATE I. 1.

(See page 311.)

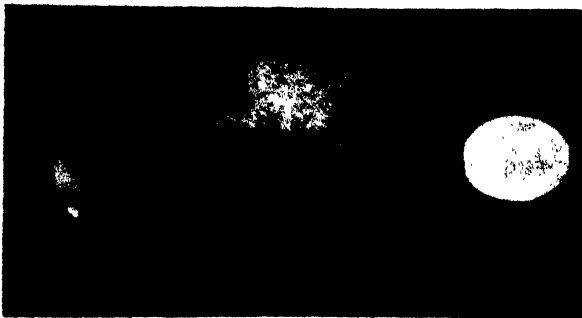


PLATE I. 2.

(See page 324.)

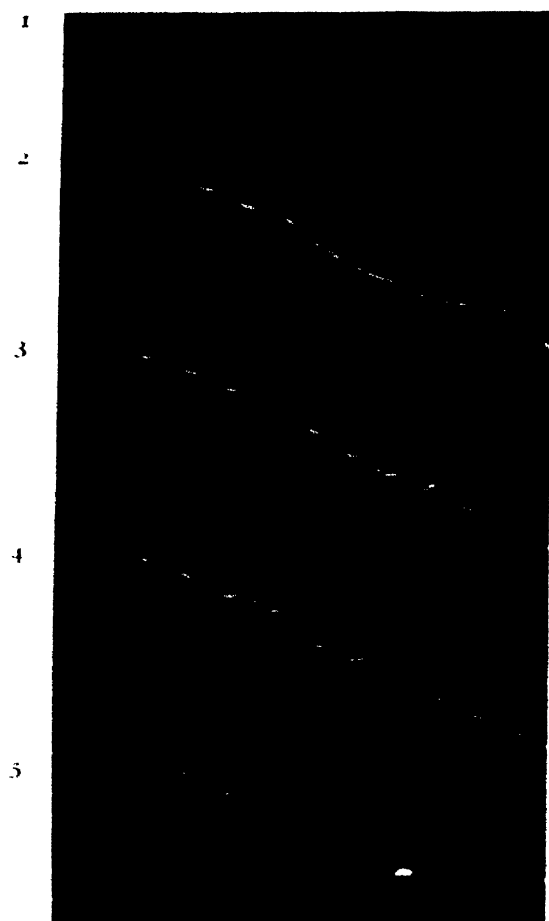


PLATE 1, 3. Densitometer curves for hydrous ferric oxide aged under water at 100°C. Time of ageing in hours: (1) 0, (2) 1, (3) 2, (4) 4, (5) 10.

To face page 301.

water in capillaries. They claim to be able to remove the latter by washing with acetone, leaving definite hydrates the composition of which depends on the conditions of drying. These claims are not justified even by Willstätter's experiments, and they are not taken seriously by many investigators (*cf.* section on stannic oxide gel).

X-ray Observations.—X-ray studies⁸ on precipitated ferric oxide confirm and extend the results of dehydration experiments. A gel thrown down at room temperature was washed free from chloride with dilute ammonia and after washing with water, separate portions were allowed to stand at room temperature and at 100°. The ageing was followed by examining samples at intervals by X-ray diffraction methods. In Plate I, 3, are reproduced the densitometer curves of the X-ray negatives for the oxide aged at 100°. These show the gradual transformation of the gel into relatively large crystals of brick-red hematite, $\alpha\text{-Fe}_2\text{O}_3$. Similar changes take place at room temperature but the progress is slower.

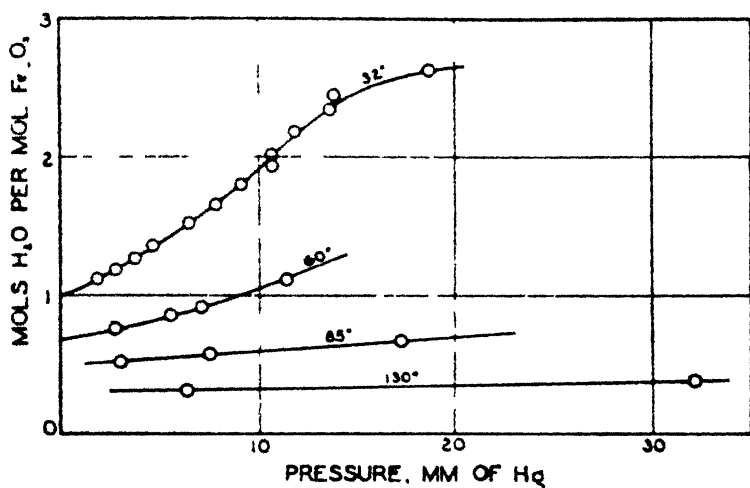


FIG. 2.—Dehydration isotherms for hydrous ferric oxide from the hydrolysis of ferric ethylate

The above observations indicate that the transformation from brown gel to brick-red precipitate consists in the growth of particles too finely divided to give a characteristic X-radiogram into crystals of $\alpha\text{-Fe}_2\text{O}_3$ large enough to give sharp diffraction lines. This growth takes place slowly at room temperature but more rapidly at high temperatures. Gels thrown down at 100° give at once the $\alpha\text{-Fe}_2\text{O}_3$ pattern and a gel precipitated at 50° and aged for a few hours at this temperature gives broad diffraction bands corresponding to $\alpha\text{-Fe}_2\text{O}_3$. It would appear therefore that the brown gel of ferric oxide contains no hydrate but consists of extremely minute particles of $\alpha\text{-Fe}_2\text{O}_3$ with adsorbed water.

Krause and his collaborators¹⁰ claim the existence of ortho- and meta-hydroxides of iron as well as a variety of products of ageing from a procedure which involves the synthesis of silver ferrites. Krause assigns definite molecular structures to the freshly formed gels and interprets the changes as a result of polymerisation, ring closure, aggregation, oxygen

¹⁰ *Z. anorg. Chem.*, 1932, 204, 20, 385; 206, 328; 208, 282; 1933, 211, 98; 216, 577; 1934, 219, 203, 213.

bridging, etc. This view would appear to be of limited applicability even if one grants that the evidence demands such a formulation as Krause proposes for those gels which are too finely dispersed to give the α - Fe_2O_3 diffraction pattern.

The Alumina Gel.

The constitution of the gel thrown down from an aluminum salt with ammonia has been the subject of considerable controversy since Willstätter and Kraut¹¹ claimed to get a series of definite hydrates by precipitating aluminum sulphate with ammonia under varying conditions. A precipitate which Willstätter prepared by mixing 1 l. of 1 *N* $\text{Al}_2(\text{SO}_4)_3$ at 100° and 1 l. of 6 *N* NH_4OH at 50°, followed by conducting in steam for five hours, was a pale yellow plastic mass *A*; without the steam treatment, it was a very pale yellow plastic mass *B*; with more dilute ammonia it was a pure white, very voluminous, and very finely divided substance, *C*. An intermediate variety *b*, prepared by the dialysis of aluminum chloride with frequent additions of small quantities of ammonia, was claimed to be related chemically to *B* but resembled *A* in adsorptive power; a modified form of *C* precipitated at 60° had an adsorptive capacity similar to *B*; and a new form of *A*¹² claimed to be $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ was obtained by carrying out the precipitation at approximately 50°, washing by decantation four times, followed by the addition of 15 per cent. ammonia and further washing by decantation until peptisation started. As a result of dehydration experiments with the gels, Willstätter claimed to get various hydrates which gave certain temperature intervals of almost constant water content. Thus precipitates obtained at low hydroxyl ion concentration and washed with acetone which was tacitly assumed to remove adsorbed water, analysed approximately for trihydrate; and precipitates obtained with excess ammonia in the hot gave what were assumed to be poly-aluminum hydroxides such as $2\text{Al}(\text{OH})_3 \cdot \text{H}_2\text{O}$, $4\text{Al}(\text{OH})_3 \cdot 3\text{H}_2\text{O}$, and so on up to $8\text{Al}(\text{OH})_3 \cdot 7\text{H}_2\text{O}$. X-ray analysis of the several preparations in the author's laboratory¹³ showed that most of Willstätter's alleged hydrates have no existence in fact. Thus the preparations *A*, *B*, *C*, and new *A* all gave the X-ray pattern of the monohydrate, $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$.

Since the gels formed by Willstätter's procedures by precipitation at 50° or above are hydrous $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$, it seems probable that the gels thrown down at room temperature are likewise hydrous monohydrate. In support of this Rooksby¹⁴ obtained diffuse $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ lines from a gel thrown down at room temperature and Havestadt and Fricke¹⁵ found the same thing for a gel precipitated at 0° and washed eight hours by decantation.

On ageing at room temperature hydrous $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ goes over spontaneously into the metastable trihydrate $\alpha\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ or bayerite and thence to the stable $\gamma\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ or gibbsite. Since the X-ray diffraction patterns of trihydrates obtained by different people are not always the same but are similar in certain respects to the gibbsite pattern, we believed at one time that the samples were mixture of $\gamma\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$

¹¹ *Ber.*, 1923, **56B**, 149, 1117; 1924, **57B**, 1082; 1925, **58B**, 2451.

¹² Willstätter, Kraut, and Humme, *Ber.*, 1931, **64B**, 1697.

¹³ Weiser and Milligan, *J. Physic. Chem.*, 1932, **36**, 3010; cf. Biltz and Lehrer *Z. anorg. Chem.*, 1928, **172**, 304.

¹⁴ *Trans. Ceram. Soc. England*, 1929, **28**, 399.

¹⁵ *Z. anorg. Chem.*, 1930, **188**, 357.

and $\alpha\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ in varying proportions. It is now known,¹⁶ however, that samples of the metastable isomer $\alpha\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ are likely to contain more or less of the stable isomer, and that this apparently accounts for the differences in the bayerite patterns obtained by different investigators and the presence in them of lines corresponding to $\gamma\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. In a study of the transformation from monohydrate to trihydrate by isobaric dehydration and X-ray diffraction methods, Hüttig¹⁷ was led to conclude that a continuous series of crystalline hydrates between the two extreme compositions are formed. It is much more probable that the intermediate products were not definite chemical individuals as Hüttig suggests but were mixtures of $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$, $\alpha\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ and $\gamma\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ in varying amounts depending on the conditions of precipitation and the age and treatment of the sample.

Although the existence of $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ has been definitely established it does not give a "step" dehydration isobar. Moreover, in the dehydration of gibbsite, $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ is formed as an intermediate product but one would never know it from the form of the dehydration isobar which gives no break corresponding to the monohydrate. Finally the X-ray diffraction pattern for γ -monohydrate persists below a composition corresponding to $\text{Al}_2\text{O}_3 \cdot 0.35\text{H}_2\text{O}$. The cause of this anomalous behaviour in the dehydration of alumina gel and of alumina trihydrates calls for special consideration.¹⁶

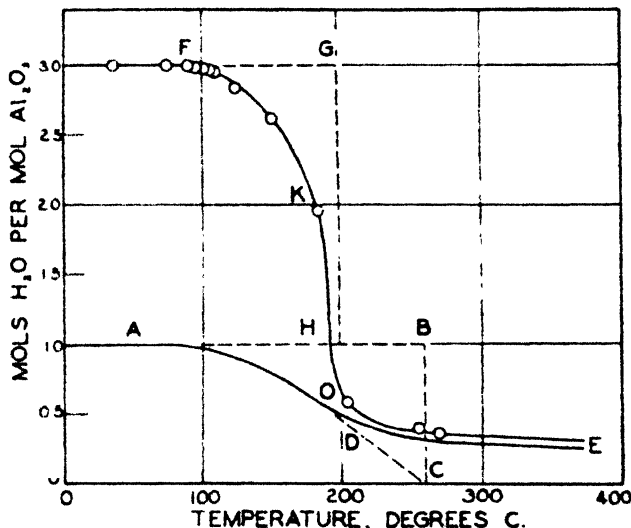


FIG. 4.—Dehydration isobars for $\gamma\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$.

Application of the phase rule to the two-component system hydrate-oxide-water vapour, shows that the system should be univariant. The type of isobar is given by the lines AB and BC in Fig. 4. Theoretically, the curve should drop to zero composition at a definite temperature, but actually the isobars are usually rounded off as shown in the figure by the line ADC . This is due to loss of part of the water below the true decomposition temperature of the mass of the hydrate on account of lattice distortion, strain in the crystals, and variation in crystal size. Now if the oxide formed by the dehydration of the hydrate is highly hygroscopic, it will adsorb most of the water vapour. Hence the actual dehydration measured is the loss of adsorbed water from the oxide. In such cases a bivariant type of curve is to be expected, as shown by the

¹⁶ Weiser and Milligan, *J. Physic. Chem.*, 1934, **38**, 1175.

¹⁷ Hüttig and Wittgenstein, *Z. anorg. Chem.*, 1928, **171**, 329; Hüttig and Kostelitz, *ibid.*, 1930, **187**, 11.

solid line *AE* in Fig. 4. It is precisely this last type of curve which Fricke and Severin¹⁸ obtained for both α - and γ - $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$.

The loss of water by a hydrate below a definite decomposition temperature is attributed by Damerell¹⁹ to surface dehydration of extremely minute crystals, without lattice rearrangement. This view is unsatisfactory since one gets a similar form of curve even with macroscopic crystals. As already pointed out, Hüttig explains the absence of sharply defined steps in the dehydration isobars of hydrates by postulating that a part of the definite hydrate water is "osmotically bound." This view appears less tenable in the case of definite hydrates than in the case of gels of the anhydrous oxides.

We can now explain the persistence of the X-radiogram of the monohydrate where it would ordinarily not be expected to exist. The X-radiogram for the monohydrate should persist along the broken curve *ADC* because some monohydrate exists as such and the extremely hygroscopic γ - Al_2O_3 formed by partial decomposition of the former is either amorphous or too finely crystalline to be detected by X-ray analysis.

In a higher hydrate decomposing first into a lower hydrate and finally into the anhydrous substance, it is apparent that, under the conditions noted above, the isobar will fail completely to detect the lower hydrate. In Fig. 4 the theoretical curves for the case of a trihydrate decomposing to a monohydrate and this in turn to the oxide are given by the broken lines *FGHBC*. The actual experimental curve as obtained by Weiser and Milligan¹⁶ is given by the solid line. The composition of the trihydrate remains constant until at point *F* some water is lost, giving a small amount of water vapour and monohydrate. As this process continues along *FKH*, all the trihydrate decomposes rapidly, giving monohydrate. Now at this temperature the lower hydrate loses water to point *O*, and hence the line *FKH* continues past the theoretical composition of the monohydrate to the point *O*. This decomposition of the monohydrate gives the highly adsorptive γ -oxide, the presence of which causes the dehydration to proceed along the line *HOE* for the reason given above.

Stannic Oxide Gel.

By drying different precipitated stannic oxides under suitable conditions, a number of supposedly definite oxide hydrates were formed. The vapour pressure isotherms of van Bemmelen¹ failed to establish the existence of any definite hydrate in the gel and suggested that compositions corresponding to a hydrate were purely accidental. Van Bemmelen's observations were confirmed and extended and his conclusions reaffirmed by Lorentz,²⁰ Mecklenburg,²¹ and Weiser.²² In recent years, however, Willstätter and his collaborators²³ adopted the older view that the behaviour of the variety of oxides could be explained best by assuming the existence of more or less stable hydrates. Willstätter claimed to remove all the adsorbed water from a compound by

¹⁸ *Z. anorg. Chem.*, 1932, 205, 287.

¹⁹ Damerell, *J. Physic. Chem.*, 1931, 35, 1061; Damerell, Hovorka, and White, *ibid.*, 1932, 36, 1255.

²⁰ *Z. anorg. Chem.*, 1895, 9, 369.

²¹ *Ibid.*, 1909, 64, 368; 1912, 74, 207; 1913, 84, 121.

²² *J. Physic. Chem.*, 1922, 26, 654.

²³ *Ber.*, 1924, 57B, 63, 1491; 1926, 59B, 2541; *Kolloid-Z.*, 1929, 49, 353.

drying rapidly in vacuum or by leaching with acetone. The composition of a gel formed in a special way, and dried by the acetone method at -35° to $+10^{\circ}$, was represented by the formula $\text{Sn}(\text{OH})_4 \cdot \text{H}_2\text{O}$; but when dried at room temperature the analysis showed a composition $\text{Sn}(\text{OH})_4$, which was regarded as the first member of a series of α -stannic acids. In an aqueous medium, $\text{Sn}(\text{OH})_4$ was supposed to go over into other less basic members of the series. Thus by suitable conditions of precipitation and drying with acetone at 0° to 10° , orthodistannic acid was supposedly formed; at 35° to 46° , orthotristannic acid; and so on. Different so-called β -stannic acids were likewise prepared and many of them assigned formulas.

As proof of hydrate formation, Willstätter cites the regions of almost constant water content in the temperature-composition curves of acetone-dried preparations. Such evidence is altogether inconclusive, particularly when the nature and location of the "flats" in the curves are determined almost exclusively by the history of the sample. The same may be said of the "flats" in the vapour pressure curves of van Bemmelen. The adsorptive capacity of a hydrous oxide for water at different stages of dehydration is determined by the physical character of the preparation; hence a "flat" corresponding to a definite hydrate is purely accidental and can be duplicated only by following a set method of procedure in precipitation, ageing, and drying. Willstätter's comparison of the behaviour of hypothetical, high-molecular, hydrated, stannic acids with their groups $\text{Sn} : \text{O}$ and $\text{Sn} : \text{OH}$, to that of carbohydrates with the groups $\text{C} : \text{O}$ and $\text{C} : \text{OH}$, appears highly fantastic and illusionary. As Posnjak²⁴ points out: "Willstätter and his collaborators did not bring forth a single new fact, but rather take the problem back some fifty years and only add to the confusion."

Fortunately, Posnjak was able to settle the question of the composition of the so-called α - and β -stannic acids by the aid of X-ray diffraction analysis. Samples of the so-called α - and β -oxides were found to give identical diffraction patterns which in turn were identical with that of the mineral cassiterite—anhydrous stannic oxide. This result has been confirmed by Förster²⁵ and by Hüttig and Döbling,²⁶ so that the facts are quite well established. The α - and β -stannic oxides are not isomers but are structurally the same: stannic oxide with more or less adsorbed water. The differences in properties are due to the size and extent of coalescence of the primary particles into secondary aggregates. Similar conclusions were reached by Pascal²⁷ from measurements of the molecular susceptibilities of various preparations.

In spite of the conclusive nature of the evidence against the existence of isomeric forms and hydrates of stannic oxide, Thiessen and Koerner²⁸ claim that a stannic oxide gel prepared by the slow hydrolysis of an alcoholic solution of stannic ethylate gives pressure-temperature and composition-temperature curves that indicate the formation of no less than six definite hydrates. This could not be confirmed in the author's laboratory²⁹ as shown by the dehydration isobar given in Fig. 5, together with similar isobars for typical α - and β -oxides. In every case, smooth

²⁴ *J. Physic. Chem.*, 1926, **30**, 1073; Yamada, *J. Chem. Soc. Japan*, 1923, 44, 210.

²⁵ *Physik. Z.*, 1927, **28**, 151; Havestadt and Fricke *Z. anorg. Chem.*, 1930, 188, 357.

²⁶ *Ber.*, 1927, **60B**, 1029; Gutbier, Hüttig and Döbling, *ibid.*, 1926, **59B**, 1232.

²⁷ *Compt. rend.*, 1922, **175**, 1063.

²⁸ *Z. anorg. Chem.*, 1931, **195**, 83.

²⁹ Weiser and Milligan, *J. Physic. Chem.*, 1932, **36**, 3030.

curves were obtained indicating the absence of hydrates. The change in direction at a temperature of 60° - 70° with the oxide made by Thiessen and Koerner's method is not due to a hydrate but to the presence of adsorbed alcohol in the sample. The breaks in the curves of Thiessen and Koerner appear to be the result of faulty technique, possibly the failure to allow sufficient time for equilibrium to be established under

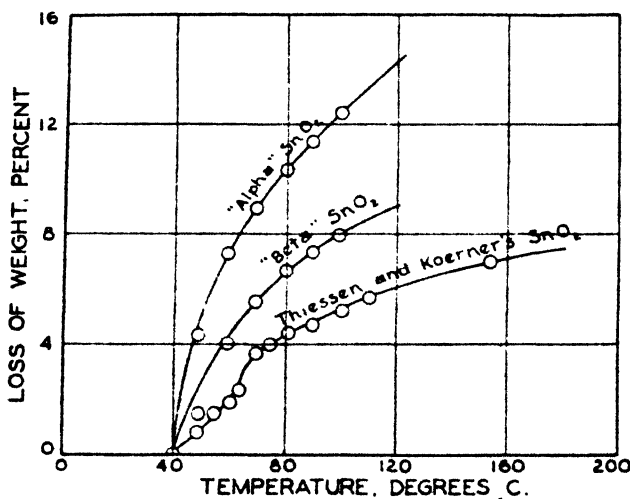


FIG. 5.—Dehydration isobars for hydrous stannic oxides.

a given set of conditions. Finally, X-ray diffraction patterns of samples obtained by dehydrating Thiessen and Koerner's gel at definite temperatures, show that no definite hydrates are actually formed: the several alleged hydrates were found to consist of stannic oxide (cassiterite) of varying particle size

with varying amounts of adsorbed water.

From the above and other similar observations it is concluded that, for the most part, gelatinous precipitates of the oxides are not polymerised bodies or condensation products resulting from the splitting off of water from hypothetical metallic hydroxides. Instead, they are believed to consist of an agglomerate of extremely minute crystals of oxide or of a simple hydrate (or hydroxide) which holds large amounts of water by adsorption and capillary forces.

Hydrous Oxide Sols.

Hydrophobic sols such as those of the hydrous oxides can be prepared fairly free from electrolytes but it was demonstrated first by Thomas Graham and confirmed repeatedly thereafter, that in the absence of protecting colloids, some electrolyte must be present in the sols to ensure their stability. Thus ferric oxide sol formed by hydrolysis of ferric chloride or by peptisation of the hydrous oxide by ferric chloride always contains traces of chloride however long the dialysis is continued.

The presence of chloride in the dialysed sols led Wyruboff and Verneuil³⁰ to suggest that the various preparations contain basic salts or chlorides of "condensed" hydroxides. This idea was further extended and developed by several investigators especially by Duclaux, Malfitano, Hantzsch and Desch, and Linder and Picton. The view that the oxide sols are oxy salts or basic salts meets with serious objection at the outset since definite chemical oxychlorides or basic chlorides are seldom encountered. No oxychloride of aluminium has been established with

³⁰ *Bull. soc. chim.*, 1899, (3), 21, 137.

certainty and but one ferric oxychloride has been identified, the compound FeOCl prepared by Stirnemann³¹ by heating a solution of ferric chloride in a bomb tube between 270° and 410° . The idea that Graham's ferric oxide sol contains a basic salt gained support from Böhm's³² observation that the particles in an aged sol gave an X-radiogram for a basic salt identical with that said to be obtained by the slow hydrolysis of ferric chloride. It has been established³³ however, that the alleged basic salt is in reality $\beta\text{-Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ with varying amounts of adsorbed chloride depending on the conditions of formation and the treatment.

Pauli³⁴ considers the colloidal particles to be complex colloidal ions resulting from ionisation of complex electrolytes allied to the Werner compounds. Since the constitution of a given sol varies with the conditions of preparation, he represents it by a general formula. In the case of ferric oxide sol this is $(x\text{Fe}(\text{OH})_3 \cdot y\text{FeOCl} \cdot \text{FeO})^+$, Cl^- in which $x = 32$ to 350 and $y = 2.16$ to 18 in sols formed by peptisation and $x = 33$ to 150 and $y = 4$ to 5.7 in sols formed by hydrolysis. It is difficult to justify this formulation since no one has established the existence of $\text{Fe}(\text{OH})_3$, and FeOCl is obtained only under special conditions in a bomb tube at elevated temperatures.

Thomas and co-workers³⁵ suggest that the dispersed phase in hydrous oxide sols such as alumina sol formed by peptisation of the gel with hydrochloric acid, consists of olated and possibly oxolated aluminum oxychloride complexes of the Werner type resembling the poly-ol basic salts formulated by Bjerrum. This assumption was made to account for the observation that the p_{H} value of the sol is raised by the stepwise addition of neutral electrolytes, the anion order being: oxalate > acetate > sulphate > halides > nitrate. The increased p_{H} value was attributed to replacement of OH groups by the anion of the added salt, followed by the union of the displaced OH radicals with hydrogen to form water.

Since hydrous oxide sols formed in the presence of chloride, say, always contain more or less chloride, Thomas believes that such sols should be designated as metallic oxychloride sols rather than as hydrous oxide sols. He recognises that the term ferric oxychloride hydrosol is objectionable since it connotes a definite chemical compound when no such meaning is intended. Nevertheless he prefers to regard the hydrous oxide sols as oxysalt sols since the colloidal particles are not pure hydrous oxides. To be consistent, one should rename the metallic sols and the salts sols which like the oxide sols are not pure insoluble metal or salt. It is difficult to see what would be gained by introducing such a change in our terminology. The ratio of iron to chlorine in a ferric oxide sol has been variously reported as 6, 42, 84, 396, 2700 and higher. To designate a sol with a low chloride content as an oxychloride sol is like calling precipitated barium sulphate a chlorosulphate because it contains some adsorbed barium chloride.

It is now quite generally recognised that the stability of a positive silver halide sol is due to the preferential adsorption of silver ion by unsaturated secondary valence forces on the surface of the crystals. The

³¹ *Neues. Jahrb. Mineral., Geol.*, 1925, **52A**, 356.

³² *Z. anorg. Chem.*, 1925, **149**, 219.

³³ Weiser and Milligan, *J. Am. Chem. Soc.*, 1935, **57**, 438.

³⁴ Pauli-Valko, *Elektrochemie der Kolloide*, 1929.

³⁵ *J. Physic. Chem.*, 1931, **35**, 27; *J. Am. Chem. Soc.*, 1932, **54**, 841; 1934, **56**, 794, 1844.

crystals will also contain some adsorbed silver nitrate. Similarly a hydrous oxide sol formed in the presence of metallic chloride, hydrochloric acid, and their corresponding ions, will contain varying amounts of the several components depending on the precise method of formation and the purification of the sol. The positive charge on a given sol is due to the preferential adsorption of hydrogen and metallic ion on the surface of the hydrous oxide just as the positive charge on a silver halide sol is due to preferential adsorption of silver ion. It is unnecessary to attribute the charge to the presence of an "ionogenic complex attached to the surface" (Pauli) unless the presence of such a complex has been rendered highly probable. Thus to assume the presence of even a simple salt like FeOCl in a ferric oxide sol goes well beyond the established facts.

Some light has been thrown on the constitution of hydrous oxide sols, indirectly from observations of the phenomena which occur during the coagulation by electrolytes and directly from X-ray diffraction studies. These will be illustrated by a few specific examples.

Titration of Sols with Salts.

Linder and Picton³⁶ showed that chloride ion passes into solution by exchange with sulphate when a ferric oxide sol prepared from ferric chloride is coagulated by potassium sulphate. This observation has been confirmed and extended by Pauli³⁷ who regards the precipitation process as a chemical reaction with the formation of an insoluble salt which he formulates as follows: $2[(x\text{Fe}(\text{OH})_3 \cdot y\text{FeOCl} \cdot \text{FeO})\text{Cl}] + \text{K}_2\text{SO}_4 = [x\text{Fe}(\text{OH})_3 \cdot y\text{FeOCl} \cdot \text{FeO}]_2\text{SO}_4 + 2\text{KCl}$. Such a formulation fails to take into account the fact that the alleged insoluble chlor-sulphate does not precipitate like simple insoluble compounds do, but comes down all at once after a critical concentration of sulphate is added. This and other phenomena observed when precipitating electrolyte is added stepwise to the sol indicate the inadequacy of the solubility theory.

In the coagulation of positively charged sols formed from metallic chloride, the precipitating anion is taken up by the particles in exchange with chloride. Rabinovich and Kargin³⁸ followed the change in the chloride ion concentration potentiometrically on adding sulphate and other anions stepwise to a definite amount of sol. Since they failed to allow time for equilibrium conditions to be established, erroneous conclusions were drawn from their observations.³⁹ To overcome this objection the following procedure has been employed in the author's laboratory:⁴⁰ Pure freshly precipitated calomel was suspended in the aged hydrous oxide sol. A 20-c.c. portion of the sol was placed in the outer compartment of a glass mixing apparatus and a definite amount of electrolyte diluted to 5 c.c. in the inner compartment. After mixing, the mixture was transferred to a small bottle which was kept in the thermostat at 25° for 2 days, shaking at intervals to saturate with calomel. The mixture was then placed in an electrode vessel consisting of a 30 c.c. weighing bottle in the bottom of which was sealed a platinum

³⁶ *J. Chem. Soc.*, 1905, 87, 1908.

³⁷ Pauli and Matula, *Kolloid-Z.*, 1917, 21, 49; Pauli and Rogan, *ibid.*, 1934, 35, 131; Pauli and Walter, *Kolloid-Beihfte*, 1923, 17, 256.

³⁸ *Z. physik. Chem.*, 1928, 133A, 203; Rabinovich and Fodiman, *ibid.*, 1932, 159A, 403.

³⁹ Weiser and Gray, *J. Physic. Chem.*, 1932, 36, 2178.

⁴⁰ Weiser, *J. Physic. Chem.*, 1931, 35, 1, 1368.

wire making contact with mercury in the bottom of the vessel. After 24 hours the potential of the resulting half-element was measured against

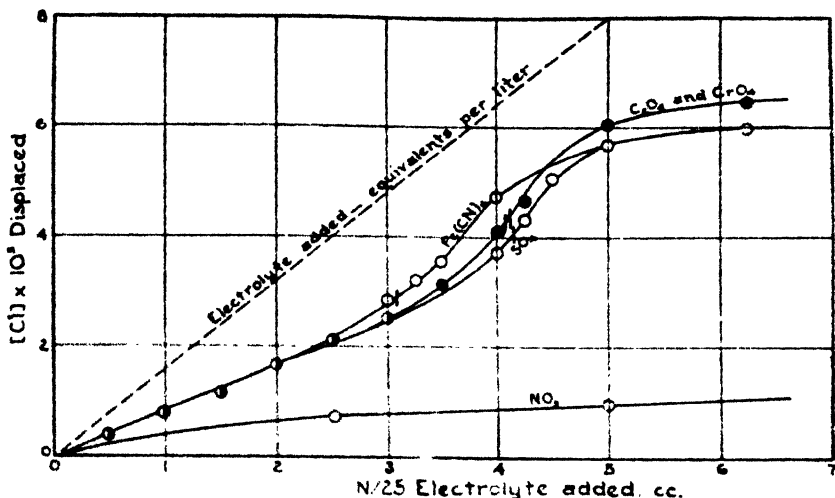


FIG. 6.—Titration curves for ferric oxide sol with electrolytes.

a standard calomel electrode. A series of such half-elements was made with the amount of electrolyte increasing stepwise. Some observations on the titration of a ferric oxide sol containing 435 millimols Fe_2O_3 and

16.6 millimols Cl per litre are shown in Fig. 6. Similar observations were made on alumina sols and, at the same time, the change in the pH value following the stepwise addition of electrolyte was determined. Typical results are illustrated in Figs. 7 and 8. In Fig. 7 are given the titration curves with $\text{K}_2\text{C}_2\text{O}_4$ for an alumina sol formed by pep-

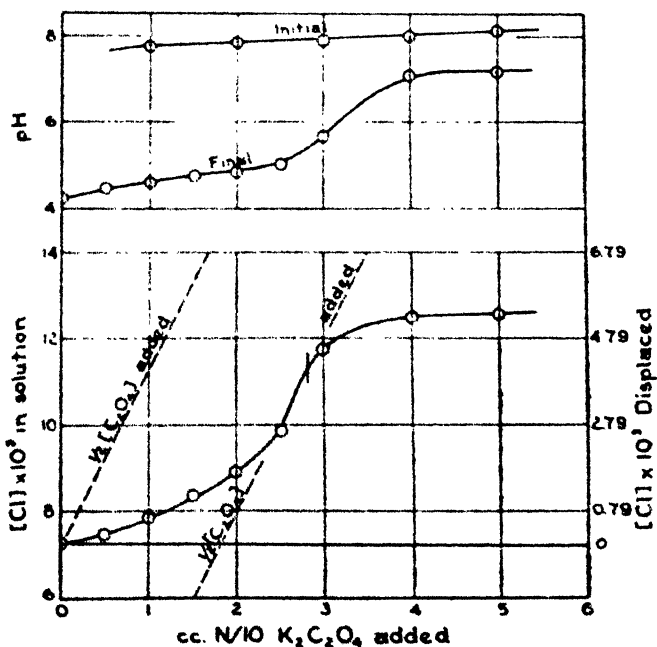


FIG. 7.—Titration curves for "grown" alumina sol.

tising "grown" alumina with dilute HCl. In Fig. 8 are given typical curves showing the simultaneous displacement of chloride and adsorption

of sulphate by a Graham alumina sol. The precipitation value is indicated by the short vertical line.

Observations of the above and other phenomena which take place during the coagulation process may be summarised as follows: (1) At the precipitation value of potassium salts of multivalent ions, the chloride in the supernatant solution is equivalent to or but little greater than the amount of added electrolyte. (2) Only a part of the chloride that is found in the supernatant solution after precipitation, can be detected potentiometrically in the original sol before adding electrolyte. Not all the chloride in the micelles is displaced by an excess of precipitating electrolyte. (3) The chloride measured potentiometrically, following

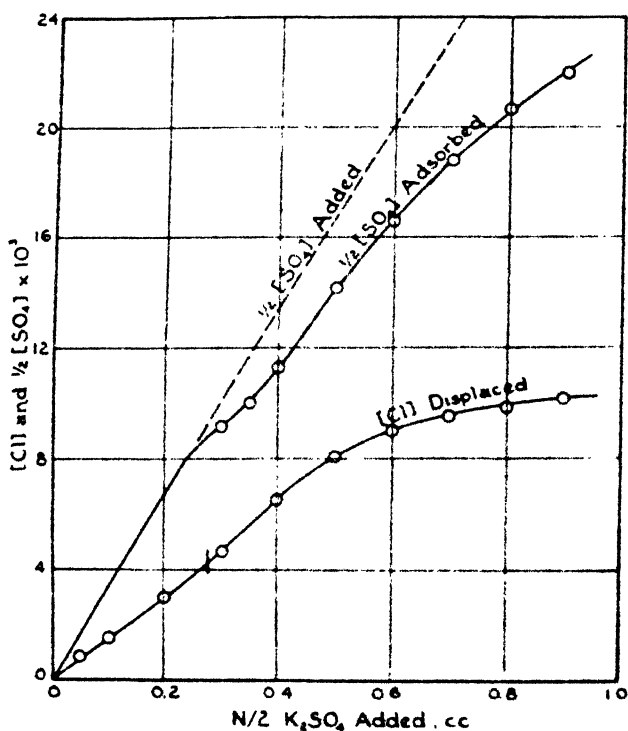


FIG. 8.—Curves showing simultaneous displacement of chloride and adsorption of sulphate on titrating alumina sol with K_2SO_4 .

the stepwise addition of electrolyte, consists of the chloride in the sol originally, together with an additional amount that is displaced when the added anion is taken up. (4) The multivalent ions investigated are taken up practically completely by the sol particles in concentrations up to and including the precipitation concentration. The chloride displaced so that it can be detected potentiometrically is less than half the amount equivalent to the multivalent ion taken up.

(5) The amount of chloride displaced follows nearly a linear course at the outset of the stepwise addition of multivalent ions but becomes proportionately greater as the precipitation concentration is approached. (6) The chloride displacement curves for multivalent ions of varying valence follow a similar course until the precipitation concentration is approached, when a marked divergence for ions of different valence is observed. (7) The three salts of divalent anions exhibit a strikingly similar behaviour as regards the entire course of the chloride displacement curves and the precipitating power. (8) The trivalent ferricyanide coagulates at a distinctly lower concentration than the divalent ions, and the chloride displaced at the precipitation value is proportionately less with the former than with the latter. (9) The chloride displacement curve with

potassium salts of univalent ions, such as nitrate, follows a course distinctly lower than that for the multivalent ions. (10) The p_H value of the sols is increased by the stepwise addition of salts, the effect being more marked with salts possessing a buffer action such as acetate, citrate, and oxalate.

To account for the above results it is assumed that the constitution of the positive sol may be represented diagrammatically as shown in Fig. 9a taking alumina sol as an example. This indicates that the particles are essentially hydrous alumina monohydrate but since they contain some chloride that is difficult to displace the composition which varies with the condition of formation is represented by some point in the three component diagram $Al_2O_3 \cdot H_2O \cdot HCl$ which may be represented symbolically as $xAl_2O_3 \cdot H_2O \cdot yHCl \cdot zH_2O$. Since the oxide shows such a strong tendency to adsorb aluminum and hydrogen ions as com-

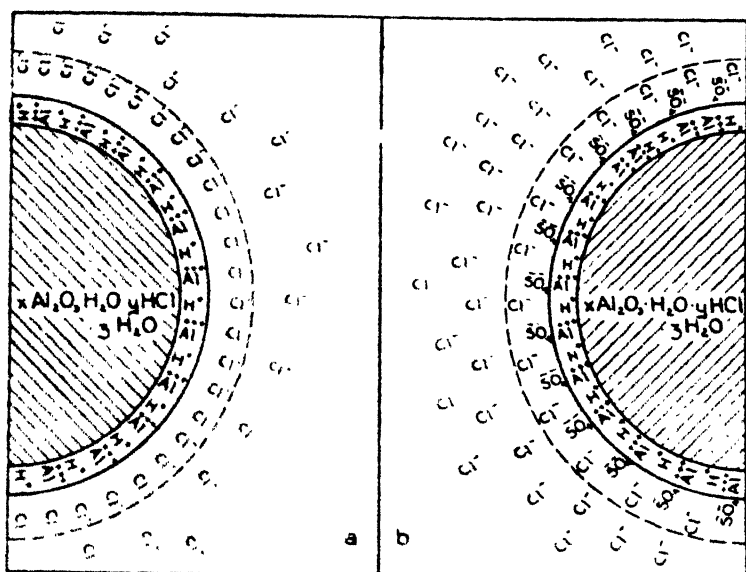


FIG. 9.—Diagrammatic representation of the constitution of alumina sol: (a) before and (b) after the addition of sulphate.

pared with chloride, the particles are surrounded by an ionic double layer with the cations in the inside and chloride on the outside. The inner portion consists of adsorbed aluminum and hydrogen ions in adsorption equilibrium with the corresponding cations in the intermicellar liquid. The outer portion consists of a diffuse layer⁴¹ of chloride ions most of which are held by the electrostatic attraction of the adsorbed positive inner layer but a part of which, because of relatively higher kinetic energy exert sufficient osmotic repulsive force against the attraction of the inner layer to influence the calomel electrode and so may be detected potentiometrically. The latter are represented in the diagram beyond the dotted circle.

This diagrammatic representation of the structure of the micelles indicates (1) its variability in composition as regards its water and chloride content, (2) the source of its positive charge, and (3) the reason only a part of the chloride can be detected potentiometrically.

⁴¹ Gouy, *J. Physique*, 1910, (4), 9, 457.

On adding a coagulating electrolyte such as potassium sulphate to the sol, the divalent sulphate being more strongly adsorbed than chloride forces itself into the double layer closer to the adsorbed hydrogen and aluminum ions as indicated diagrammatically in Fig. 9b. Potentiometric analysis enables one to determine the chloride displaced. The difference between the chloride in the sol originally and that after the addition of sulphate, in other words, the displaced chloride, is not equivalent to the adsorbed sulphate since a part of the sulphate which enters the layer corresponds to chloride measurable potentiometrically in the original sol.

The adsorbed sulphate lowers the potential on the particle in the following way: A sulphate ion has the same average kinetic energy as a chloride ion but it possesses double the charge. Accordingly, if one assumes for the moment that the valence only determines the adsorbability, the divalent particles in the outer layer would be drawn closer to the inner layer and the thickness of the double layer would be decreased. Since the potential difference between two layers of opposite sign with constant charge density is directly proportional to the distance between them, it follows that the reduced thickness of the layer will be accompanied by a decrease in potential on the particle.

Since with ferric oxide sol the three divalent ions: sulphate, oxalate, and chromate, exhibit such a strikingly similar behaviour in displacing chloride and in reducing the potential to the coagulation value, it follows that with these three ions the valence is the most important factor determining the adsorbability.

The behaviour of trivalent ions such as ferricyanide would follow from what has been said. The ions having the same average kinetic energy but with three charges will be drawn closer to the inner layer than the divalent ions, and the further reduction in thickness of the double layer manifests itself in a lower precipitation value. The chloride ion displaced is obviously less, since less ferricyanide than divalent ion needs to be adsorbed to lower the charge on the particles to the coagulation value.

The adsorption of both the divalent and trivalent ions is sufficiently great that the amount necessary to cause coagulation is practically completely adsorbed.

The lowering of the potential on the particles results in coalescence and agglomeration of the particles with a consequent decrease in specific surface. This manifests itself in an increase in the amount of chloride displaced for a given increment in the multivalent ion added as the region of rapid coagulation is approached. Hence the upward bend in the chloride-displacement curve with multivalent ions, becomes more marked in the region of rapid coagulation. Above the coagulation point, the chloride is displaced from the precipitate by exchange adsorption without any marked decrease in specific surface, and the curve follows the usual course of the adsorption isotherm. This combination of conditions accounts for the S-shape of the chloride-displacement curve with all electrolytes having a high precipitating power and causing rapid coagulation above a critical concentration.

The increase in the p_H -value of hydrous oxide sols on adding a neutral salt especially those with multivalent anions, is doubtless due chiefly to the increased adsorption of hydrogen ion in the presence of a strongly adsorbed anion. This increased adsorption of cations in the presence of strongly adsorbed anions is a general phenomenon that has been observed

with various types of adsorbents such as carbon and fibres as well as with the hydrous oxides. With salts such as citrates, oxalates and acetates, buffer action increases the p_H value of the sol-electrolyte mixture above that of the sol alone. Iyer⁴² accepts our formulation of the constitution of certain oxide sols but suggests that the outer layer may contain hydroxyl ions as well as chloride ions. The displacement of the former on titrating with neutral salts would account for the increase in p_H value of the mixture.

X-ray Diffraction Studies.

Since X-ray diffraction studies have proven helpful in determining the composition of gels it was believed that similar studies on sols might give direct evidence of the constitution of the colloidal particles in the sols. The chief complication in the examination of such systems is the relatively low concentrations of the solid phase and the scattering of the X-rays by the water in the samples. Böhm and Niclassen⁴³ showed that the gels from certain oxide sols were not amorphous but in most cases it was not stated whether the air-dried or moist gel was examined. Since Thomas believes that the elements of water in certain oxide sols are combined in the form of poly-ol basic Werner salts, it is not permissible to air-dry the samples before examination. On the contrary, the sols must be studied directly, or the undried gel obtained preferably by ultrafiltration of the sols must be examined. The first experiments were carried out with the gels obtained by ultrafiltration of the following typical sols: (1) Hydrous alumina sols formed by peptisation with hydrochloric acid of (a) the gel thrown down at 100° from aluminum chloride solution with ammonia, and (b) the gel formed by the action of hot water on amalgamated aluminum. Thomas' procedure in making the sol from amalgamated aluminum was employed. (2) Hydrous stannic oxide sols prepared by the method of Zsigmondy. (3) Hydrous indium oxide trihydrate sol obtained by peptising the precipitated gel with hydrochloric acid.

The X-ray diffraction patterns of the moist gels were obtained in a Seemann-Bohlin type camera. Copper radiation filtered through nickel foil, at 60 milliamperes and 50,000 volts was employed. Under these conditions but 5-10 minutes exposure was necessary, so that little or no drying of the gel took place. The results of some observations are shown in diagram form in Fig. 10. From these observations it would appear that the particles in the alumina sols consist essentially of hydrous $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$. There is no reason to believe that they are made up of simple basic salts or basic salts of the Werner type. The gel from the stannic oxide sol gives the pattern of anhydrous SnO_2 (cassiterite) and that from the indium oxide sol the pattern of $\text{In}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. A thixotropic stannic oxide sol gave a good cassiterite pattern.

From the above X-ray studies, it would appear that the particles in typical oxide sols consist essentially of aggregates of minute crystals of hydrous oxides or of simple oxide hydrates. In the sols containing chloride, the latter is not bound in the form of a basic salt in most cases, but is adsorbed in amount depending on the size and physical character of the particles. Such sol systems whose constitution may be represented diagrammatically as shown in Fig. 9, are properly referred to as hydrous oxide sols.

⁴² *Proc. Indian Acad. Sci.*, 1934, 1, 372.

⁴³ *Z. anorg. Chem.*, 1924, 132, 1.

In the light of the above, if one prefers to regard the hydrous oxide sols as electrolytes with colloidal ions it must be emphasised that there is a fundamental difference between sols and non-colloidal complex electrolytes such as potassium ferrocyanide, the cobaltammines, the complex platonic salts, etc., formulated by Werner. There is also a

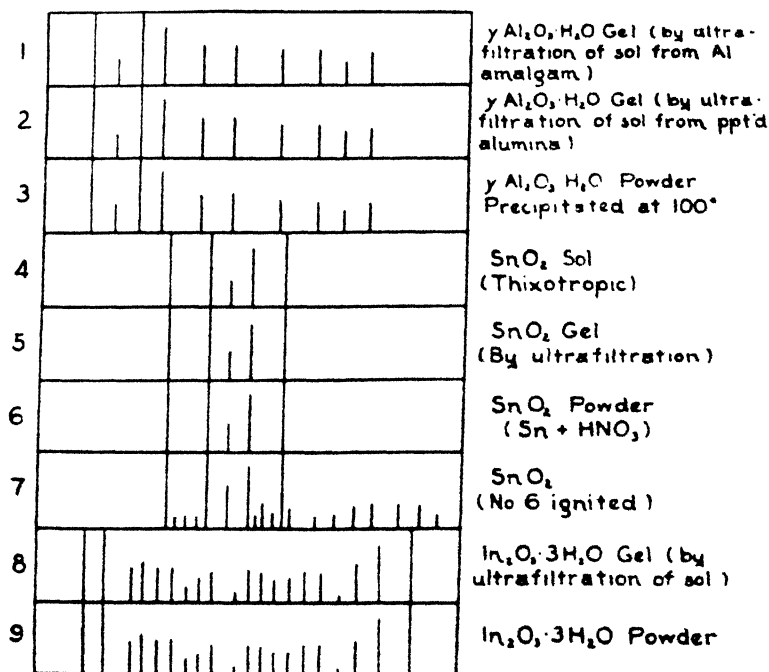


FIG. 10.—X-ray diffraction patterns for hydrous oxide gels and sols.

distinct difference between a hydrous oxide sol and such colloidal electrolytes as the soaps and Congo red in that the latter contain ionic micelles made up of groups of ions which have a definite composition and which carry one charge for each equivalent of the ion, whereas the micelles of the former have no definite composition and may carry hundreds or thousands of equivalents for each free charge.

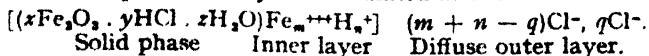
Summary.

The results of this communication may be summarised as follows:—

1. The constitution of hydrous oxide gels is deduced from experimental evidence obtained by phase rule and X-ray diffraction studies on the typical metallic oxides of iron, aluminum, and tin. The constitution of the hydrous oxide sols is formulated from the results of potentiometric studies on the titration of ferric oxide and alumina sols with electrolytes, and from X-ray diffraction studies on the hydrous oxide sols of aluminum, tin, and indium.

2. It is concluded that, in general, gelatinous precipitates of the oxides are not polymerised bodies or condensation products resulting from the splitting off of water from hypothetical unmetallic hydroxides. Instead they are believed to consist of agglomerates of extremely minute crystals of oxide or simple hydrate (or hydroxide) which hold large amounts of water by adsorption and capillary forces.

3. It is believed that the particles in typical oxide sols consist essentially of aggregates of minute crystals of hydrous oxide or of simple oxide hydrate. In sols containing chloride the latter is not bound in the form of basic salts or Werner complexes in most cases, but is adsorbed in amount depending on the size and physical character of the particles. To account for the properties of positive sols of which ferric oxide sol is typical, the constitution of the particles may be formulated as follows:



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GENERAL DISCUSSION.

Professor E. C. C. Baly and W. P. Pepper (Liverpool) (communicated):
The Hydrous Oxide Gels of Nickel and Cobalt.—In view of the important communication by Professor Weiser and Dr. Milligan some quantitative observations with the hydrous gels of nickel and cobalt may be of interest.

It was stated by Proust in 1805 that anhydrous Ni_2O_3 may be prepared by gently heating precipitated nickel carbonate in an open dish. This reaction has been investigated with nickel carbonate and hydroxide, and it has been found that, though the product is black, the Ni_2O_3 content is only from 2.4 to 4.7 per cent., the amount depending to some extent on the method of preparation. Exactly the same result is obtained when nickel carbonate is completely decomposed to NiO by heating at 250° in a high vacuum and the cooled oxide is brought into the air. If cobalt carbonate is treated in either of the above ways a quantitative yield of Co_2O_3 is obtained. It is interesting to note that when CoO , prepared by heating the carbonate in a high vacuum and allowed to cool to room temperature, is brought into the air it becomes red hot.

These facts, coupled with the fact that Ni_2O_3 is endothermic with respect to NiO , clearly indicate that the formation of Ni_2O_3 by the above methods must be due to the surface oxidation of crystal units of NiO . Since NiO is cubic, it is possible to calculate the size of these crystal units from the amount of Ni_2O_3 formed. If x be the number of Ni and O atoms in the edge of the cube, the number of atoms in the surface of the cube will be $x^2 - (x - 2)^2$, and if the oxidation be restricted to the surface atoms, the product will contain $\frac{x^2 - (x - 2)^2}{4} \text{Ni}_2\text{O}_3$ molecules, and $\frac{(x - 2)^2}{2} \text{NiO}$ molecules. Since the distance between adjacent Ni and O atoms in the cube is 2.086×10^{-8} cm., the length of the edge of the crystal unit will be $x \times 2.086 \times 10^{-8}$ cm. By this method it can be shown that 2.5 per cent. Ni_2O_3 is formed by the surface oxidation of cubes of NiO with edge of about 55μ , whilst 4.7 per cent. Ni_2O_3 corresponds to a cube with edge of about 30μ . If two surface layers be oxidised, the cubic crystal unit will have an edge twice as long.

It must be pointed out that the size of the crystal unit of NiO as determined by this method may not be that existent before the material is heated. It has been found that if the material is finely powdered before heating the amount of Ni_2O_3 in the product is rather smaller, and this suggests that during the heating the crystal units tend to increase in size owing to the loss of the adsorbed water.

The adsorption of nickel and cobalt carbonate by pure kieselguhr has also been investigated. The quantitative details will form part of a further communication dealing with the phenomenon of adsorption by kieselguhr, and the salient facts only need be recorded here. When an exactly equivalent amount of Na_2CO_3 in dilute solution is added to a suspension of kieselguhr in cold dilute $\text{Co}(\text{NO}_3)_2$ solution, the cobalt is adsorbed in crystal

units which build up a continuous crystal lattice of CoO which is three molecules thick and forms, therefore, a single adsorbed layer of elementary unit cells of CoO . This is not the case with nickel nitrate which, on the addition of Na_2CO_3 in the presence of 2 per cent. KNO_3 , appears to be progressively adsorbed in layers of single hydrous molecules of NiO . Drying the coated kieselguhr at 125° has no effect unless the surface of the kieselguhr is completely coated with three such layers when the whole deposit condenses to a continuous adsorbed crystal lattice of NiO which is three molecules thick, and thus consists of a single adsorbed layer of elementary unit cells of NiO .

If the precipitation is carried out at 100° , no adsorption by the kieselguhr takes place with cobalt. In the case of nickel only a very small proportion is adsorbed as the unit cell lattice, the remainder being not adsorbed. It may be concluded, therefore, that at room temperature the units precipitated in the first instance are single hydrous molecules of NiO and hydrous elementary unit cells of CoO , respectively. At 100° the hydrous units precipitated are larger, too large, indeed, to be adsorbed by the kieselguhr, though in the case of nickel a small proportion exists as hydrous elementary unit cells of NiO for a sufficiently long time for them to be adsorbed by the kieselguhr. This conclusion is supported by the fact that it has been proved by the oxidation method that the crystal units of NiO are larger in nickel carbonate precipitated at 100° than in the carbonate precipitated at 15° .

Dr. F. Eirich (*Wien*) said: The subject of hydrous oxide gels might be very thoroughly discussed from the point of view of the chemical constitution of the colloid particles and of colloid reactions, but I desire to refer only to one point. Pauli did not conceive colloid particles of this nature to be complex colloidal ions; he explained the preferential adsorption, which is a description rather than a definition of the process as follows: Dissociable molecules of the nature of Werner complexes are supposed to be situated on the surface of the particle, and these determine the course of the reaction. In fact the behaviour of sols is understandable if we compare it with known complex reactions. Indeed the reaction or charge of the particles is profoundly modified by variation or rebuilding of the ionogenic complexes.

The structural formula of iron oxide sols which Professor Weiser criticises was never put forward by Pauli as essentially correct. It merely describes the existence of more or less hydrated hydroxides in the core, and of chlorine ions of dissociated basic chlorides on the surface of the particle.

The pure sol prepared by Pauli and Schmitt from amalgamated aluminium had a p_{H} of 6, so that it is out of the question that hydrochloric acid could take part in the formation of these sols. The increase of the p_{H} on adding neutral salt to the sol has been explained in many papers of S. W. Pennycuik (*e.g.*, in the case of platinum sols) as due to hydrolysis of the oxide surface of the particle.

Professor K. H. Meyer (*Genève*) said: Dr. Eirich refers to the old controversy: are the ions on the surface of an inorganic particle fixed by adsorption or by complex-valencies (Pauli). I think one ought not to put the question in this form. The term "adsorption" signifies, or ought to signify, only the place, where an atom or molecule is supposed to be: at a surface or interface, and says nothing as to the forces which link the atom to the surface. These forces can be of any kind: dipole forces, electrostatic attraction, homeopolar forces (so-called activated adsorption), etc. The Pauli-theory only *specifies* the forces of adsorption, which—in many cases—according to this theory should be identical with those which exist in complex compounds.

Dr. J. H. de Boer (*Eindhoven*) said: In connection with the statement of Weiser and Milligan that the precipitates of the oxides consist of agglomerates of minute crystals, it may be of interest to mention the

existence of a special kind of aluminium oxide having half-crystalline properties lying between those of γ - Al_2O_3 and the amorphous oxide. When aluminium is oxidised electrolytically in oxalic acid or in chromic acid, an amorphous layer of Al_2O_3 is formed. It is a porous oxide layer; electrolytes can penetrate it easily. In the air this layer gives a good protection of aluminium and is used as such. When, however, aluminium is oxidised in *e.g.*, boric acid or phosphoric acid an oxide layer of quite different properties is formed. This latter layer has rectifying properties; electrolytes do not penetrate it, only aluminium ions wander through this layer and contribute to the growth of the layer on the outside. As shown by van Geel aluminium can be oxidised first in oxalic acid, where the amorphous layer is formed, and afterwards in boric acid, giving the rectifying layer beneath the amorphous one. The reverse is not possible; if the rectifying layer is made first, oxidation in oxalic acid does not give an amorphous layer under or over the rectifying one, but breaks off the rectifying layer, whereupon the amorphous one is formed free from the rectifying one.

Investigations of Verwey in our laboratory by means of X-rays have shown that the oxygen ions in this rectifying layer form already a crystal lattice but that the aluminium ions are distributed at random through this oxygen lattice. Only after heating the layer to a high temperature is the common γ - Al_2O_3 formed. We called the oxide of this layer the γ' - Al_2O_3 , it forms an intermediate state between the amorphous and the crystalline aluminium oxide as it is crystalline with respect to the oxygen, amorphous with respect to the aluminium.

Mr. C. F. Goodeve (*London*) said: Recent measurements which I have made support Dr. Weiser's contention that there is no evidence for the intermediate existence of titanium hydroxide when ammonia is added to a titanate salt. Spectro-photographs of the light scattered from a precipitate less than one second old (a flowing method was used) were found to be practically identical to those of titanium dioxide. On the other hand, there is no resemblance between the spectro-photographs of light scattered from "zinc hydroxide" and zinc oxide. This supports the X-ray evidence which indicates that zinc hydroxide has a definite existence.

Variations in the intensity of the scattered light in the wave-length region of absorption have been found and are interpreted as being due to changes in particle size. It is hoped to apply the method to the determination of the latter in a few favourable cases.

Dr. Weiser's reply is at the end of the volume.

THE CONDENSATION OF UREA AND FORMALDEHYDE.

By G. WALTER (*Vienna*).

Received in German on 16th August, 1935, and translated by
Dr. E. J. RABINOWITSCH.

Resins, which are generally mixtures of mutually soluble compounds possessing similar structures, can be divided into three groups according to their composition:—

- (1) The components are of the same analytical composition and molecular structure, differing only in the length of their molecules (Staudinger's homologous polymers).
- (2) The components are of the same composition, but are of different structure (*e.g.* isomers) and molecular size.
- (3) All three characteristics—composition, constitution and molecular size—are different.

Urea-formaldehyde resins¹ are known which belong to all these classes; but the majority are of the third and most complicated kind. The differences between the individual resins (and their components) are chiefly due to two factors: *Firstly*, to the different properties of the *primary* products of condensation of urea and formaldehyde at different relative concentrations and under different conditions; and *secondly*, to the different possibilities of further condensation or polymerisation of those primary products. These complications (as well as the insolubility of the end-products) led up to begin the investigation with the study of the conditions under which the different simple products of condensation are formed, and the isolation of these products. In the final part of the paper, the properties of the complicated resins themselves will be discussed.

I. Conditions under which the Most Important Simple Condensation-Products are Formed.

The **U.F.** condensation-products are either:

(1) *Crystallised substances*—as for instance monomethylol urea (I), dimethylol urea (II), or methylol methylene-urea (III); or

(2) *Amorphous powders*—as for instance methylene-urea $C_2H_4ON_2$, or the more highly oxidised product $C_5H_{10}O_3N_4$. A. E. Dixon² proposed the respective formulæ (IV) and (V) for the last two substances; it will be shown later (see p. 382) that these are incorrect. We shall call these substances Meth A and Meth B;

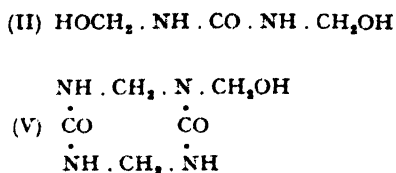
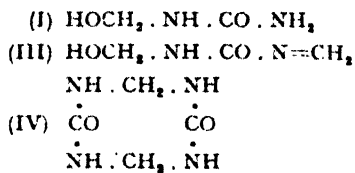
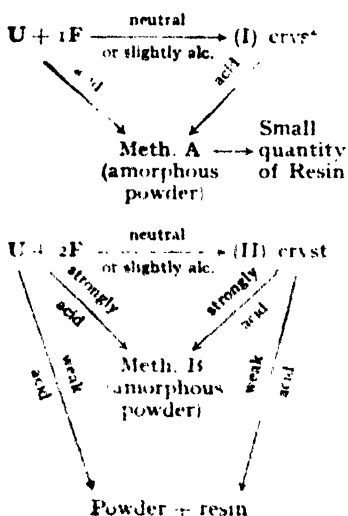
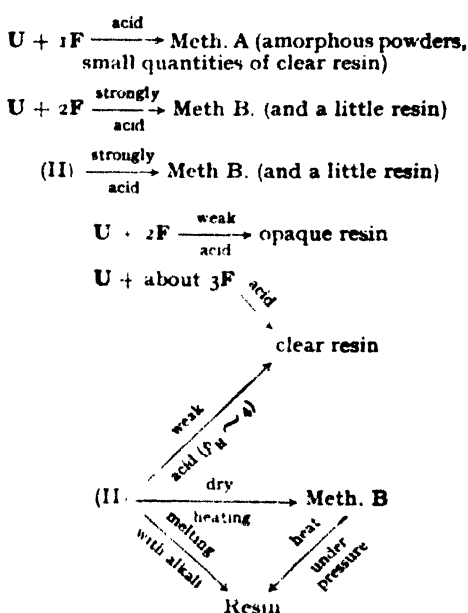
(3) *Resins*.—The composition of these products is generally complicated and unstable. It will be seen, however, that nearly pure Meth A may sometimes also appear as a resin (composed of polymers and isomers). But in general, the pure methylene ureas give "euthymorphic" products only.

The methylol compounds (I) and (II) alone are primary condensation products; all the other products can be traced back to them.

What products are actually obtained by condensation depends chiefly on the concentration of H ions (h), the temperature, and the relative concentrations of the reaction-partners **U** and **F**. In *neutral* or *slightly-alkaline* solutions water-soluble methylol-products are formed at low temperatures. In *acid* solutions, these products are further transformed into the methylene compounds, which are partly insoluble and melt at high temperatures under decomposition. The same products are obtained directly from the initial mixture of **U** and **F** in acid solution. From (I) we obtain Meth A, from (II) Meth B. Nearly pure Meth B is obtained only at high h -values (p_H = about 3) or by heating (II) above its melting-point. At low h 's, **U** and **F** in molecular proportion 1 : 2 give (at high temperature) an opaque resin. If more than three parts of **F** are used, or if dimethylol urea (II) in neutral solution is first formed, then in slightly acid solution completely transparent resins can be obtained:—

¹ The abbreviations: **U** for urea, **F** for formaldehyde will be used throughout this paper.

² The literature of the subject can be generally found in a review by G. Walter and M. Gewing, *Kolloid-chem. Beihefte*, 1931, **34**, 163-217; and in the monograph, *Die künstlichen Harze* by J. Scheiber and K. Sandig.

**Low Temperatures:****High Temperatures:**

According to this scheme, the resins are formed under conditions intermediate between those which are suitable for the preparation of the methylol and methylene derivatives respectively, and their composition lies at least partially, midway between that of these products. The first have a simple, well-known constitution; the second require special investigation.

II. Investigation of the Methylene-Urea-Compounds.

We investigated the *composition*, the *molecular weight*, and the *primary amido-groups* (end-groups) of Meth. A and Meth. B. In connection with these measurements, we also investigated the *electrical conductivity* of these substances (see the following paper) and their *viscosity*.

1. Experimental Methods.

Analysis of the Methylene-Ureas.—The following method was developed: by heating the substance with $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ in presence of conc. hydrochloric acid, the methylene and methylol groups were transformed into formaldehyde, the nitrogen² into ammonia, and the carbon of the CO-groups into carbon dioxide. This method is applicable to all derivatives of urea.

² Cf. N determination in urea with $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ after Folin, *Z. physiol. Chemie*, 1901, **32**, 305

TABLE I.

Substance.	Per Cent. CH ₃ O.		Per Cent. N ₂ .		Per Cent. C from CO.		Total C Per Cent.	
	Obt.	Calc.	Obt.	Calc.	Obt.	Calc.	Obt.	Calc.
Methyl urea . . .	—	—	37.80	37.83	16.12	16.2	—	—
Monomethylol urea .	32.7	33.3	30.79	31.10	13.17	13.3	26.3	26.6
Dimethylol urea .	49.5	50.0	22.83	23.3	9.90	10.0	29.6	30.0
Methylen urea A .	41.4	41.7	38.6	38.9	16.70	16.7	33.2	33.3
Methylen urea B .	51.4	51.8	32.0	32.2	13.75	13.8	34.3	34.5

Determination of the Primary Amido-Groups.—The NH₂-Groups were determined with the help of conc. hydrochloric acid and sodium nitrite; ⁴ this method works well with all substances of this class. The volume of N₂ evolved is measured; the reaction must be carried out *without heating*. At a higher temperature, the same method gives the *total* nitrogen-content of the molecule. The concentrated acid causes no undesirable side-reactions, as shown by the values found by analysing the most unstable of all products—the methylol ureas (I) and (II) :

TABLE II.

Substance.	In the Cold.				At High Temperature.	
	Per Cent. N.		Number of NH ₂ -Groups Per Molecule.		Total N (Per Cent.).	
	Obt.	Calc.	Obs.	Theor.	Obs.	Calc.
Methyl urea . . .	19.0	18.0	1	1	38.1	37.8
Monomethylol urea .	15.3	15.6	1	1	31.3	31.1
Dimethylol urea .	0.0	0.0	0	0	23.9	23.3

Determination of the Molecular Weight.—We found *formic acid* to be an appropriate solvent for methylene ureas and also for a number of U.F-resins. The appreciable conductivity of these solutions shows that all these urea derivatives, not unlike urea itself, are dissolved in formic acid with the production of formates. The measurements of the conductivity have a special interest in connection with the problem of the relations between conductivity and polymerisation, and will be described in full in the next paper. We used the solutions in formic acid, not only for electrolytic investigations, but also for the determination of the *molecular weight*, partly by a cryoscopic method, but mostly by Barger-Rast's method of isothermic distillation. The values of the molecular weights found by this method must be correct owing to their exact conformity with the values found by determination of the NH₂ group. No correction is required in this special case of electrolytic dissociation for directly determined molecular weights, because of molecular association or formation of ionic complexes or micelles which exactly counterbalance the influence of electrolytic dissociation.⁴ No appreciable formation of acid amides by reaction of the

⁴ Applied to urea by Stanek (see H. Meyer, *Analyse und Konstitutionsermittlung organischer Substanzen*, 1922, p. 938).

⁵ Cf. the next paper.

methylene ureas with formic acid takes place at low temperatures and consequently there is no necessity to correct the molecular weight. The change in the apparent molecular weight with time (due to a process of this kind), which is easily observed with urea itself (Table III.) does not occur with its methylene derivatives.

TABLE III.—MOLECULAR WEIGHT OF UREA IN FORMIC ACID.

At Once.	After.						
	½ Hour.	4 Hours.	8 Hours.	12 Hours.	2 Days.	3 Days.	4 Days.
58.6	55.4	52.3	50.2	48.7	44.7	42.3	39.4

2. Investigations of the Fractions of Methylene Urea.

Fractionation was effected simply by spontaneous precipitation of the methylene derivatives at $p_H = 3$. We obtained in this way three fractions, (a), (b) and (c); the fourth fraction (d), obtained by evaporation of the last filtrate, was insoluble, and therefore unsuitable for our investigation. Meanwhile, by NH_2 group determination, it was found that the fraction (d) also, although insoluble in formic acid, is low-molecular. Meth A in this respect is like

Meth B trimer. Consequently, trimers are already insoluble in formic acid, owing to the fact (compare the next paper) that the complexity of ions grows proportionately to the degree of polymerisation. In the case of the trimer, about 6 urea radicals are already united in the complex. In the case of Meth

TABLE IV.

Fraction.	Per Cent N.	Per Cent. CH_2O .	Per Cent. C. from CO_2 .	Per Cent. C. Total.
Methylene Urea A.				
(a)	38.6	41.6	16.6	33.2
(b)	38.8	41.1	16.3	32.8
(c)	38.7	41.7	16.7	33.0
$C_3H_4ON_2$ calc.	38.9	41.7	16.7	33.3
Methylene Urea B				
(a)	32.0	51.4	13.8	34.4
(b)	32.1	51.8	13.7	34.4
(c)	32.5	52.3	13.7	34.6
Calc. for $C_3H_{10}O_2N_4$	32.0	51.8	13.8	34.5

B, this fourth fraction was a resin; in that of Meth A, fraction (c) showed—quite unexpectedly—the properties of a resin. All the other fractions were amorphous powders. The analytical compositions of all products—the resins not excluded—were the same, and corresponded to the theoretical compositions of Meth A or Meth B. These results show that U. F resins, formed by methylene ureas, may sometimes have a relatively simple structure (Table IV.).

Table V. contains the experimental values of the molecular weights, the number of NH_2 -groups per mean radical (" NH_2 -number,") and the molecular weights calculated from these numbers. They are in good agreement with the values found by direct measurement.

Fractions (a), of both Meth A and Meth B, have nearly the theoretical molecular weights of the monomeric substances. The molecular weights of fractions (b) and (c) correspond roughly to those of the dimeric substances.

TABLE V.

Meth A.						Meth B.		
Molecular Weight of Monomeric Meth. A, 72. Molecular Weight of Dimeric Meth. A, 144.						Molecular Weight of Mono- meric Meth. B, 174. Molecular Weight of Dimeric Meth. B, 348.		
Fraction.	Separated After.	Per Cent. About.	M Exp.	NH ₂ Number.	M Calc.*	M Exp.	NH ₂ Number.	M Calc.*
a . .	2 hours.	20	74	0.99	73	178	1	174
b . .	17 „	40	140	0.51	141	320	0.5	348
c . .	90 „	15	148	0.43	167	338	0.5	348
d . .	—	25	—	0.34	212	—	0.3	580

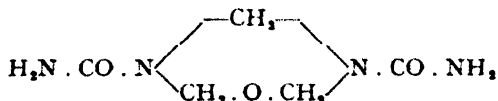
* From NH₂.

The NH₂-number is 1 for the monomeric products, and 0.5 for the dimeric ones, etc. This leads to the following formulæ:

(VI) (Meth A monomeric): H₂N . CO . N=CH₂.

(VII) (Meth A dimeric): H₂N . CO . NH . CH₂ . NH . CO . N=CH₂.

(VIII) (Meth B monomeric):



Dixon's formulæ must be wrong, because they contain no primary NH₂-groups. Formula (VIII) shows no methylol groups; in fact, no properties pointing to the existence of these groups have been observed with Meth B.

The Significance of the Molecular Weights.

Despite the relatively low molecular weight values, none of these compounds can be melted; they decompose at temperatures above 200° C. The correctness of the molecular weights seems to be ensured by the accordance between the values found by direct measurement and those calculated from the NH₂-numbers. The first fractions, (a), must thus be considered as monomeric. The values found for the other fractions can at first be taken as mean values only, and the question then arises whether those fractions contain a certain quantity of substances with a much higher degree of polymerisation; whether such substances may not be responsible for some fractions (fraction (c) of Meth A) showing the properties of a resin.

Comparative Measurements of Viscosity.—The occurrence of high polymers may reveal itself by *increased viscosity* more clearly than by a higher mean molecular weight. Experiments showed, however, that all the substances in question, and also various other substituted ureas, have about the same relatively high specific viscosity (η_{sp} in Table VI.). The high viscosity of all these compounds is apparently due to the occurrence of solvated complex positive ions,⁶ which they form with formic acid, and has therefore no bearing on our present problem. Nevertheless, the results of the viscosity-measurements seem to indicate

⁶ Cf. next paper.

TABLE VI.

Substance.	CH_3 Urea.	$(\text{CH}_3)_2$ Urea (Symm.).	$(\text{CH}_3)_3$ Urea.	C_6H_5 Urea.	$(\text{C}_6\text{H}_5)_2$ Urea (Symm.).	$(\text{C}_6\text{H}_5)_3$ Urea (Asymm.).
Concentration mols./litre)	0.021	0.020	0.029	0.020	0.022	0.023
η_{sp}	0.026	0.052	0.050	0.085	0.058	0.050

	Meth A.			Meth B.		
Substance.	Fraction a.	Fraction b.	Fraction c.	Fraction a.	Fraction b.	Fraction c.
Concentration (mols./litre)	0.026	0.026	0.026	0.022	0.022	0.022
η_{sp}	0.055	0.063	0.005	0.063	0.079	0.077

These experiments contributed another argument against the presence of highly-polymerised substances in the fractions (b) and (c). They revealed that, by heating the dried methylene ureas, the degree of polymerisation is appreciably increased only in the case of the monomeric fraction. On heating, the molecular weight approaches that of the dimer. The molecular weights of (b) and (c) are changed only very slightly, and only if they were below the dimeric values before heating. The molecular weights of all fractions are thus brought by heating to, or slightly above, that of the dimer (Table VII.). Were the fractions (b) and (c) to consist of a mixture of the monomer with a small quantity of high polymers, we should expect their molecular weights to increase appreciably on heating. This is not the case. We tried to *extract* the

Fraction.		Methylene-Urea A.								Methylene-Urea B.							
		a.		b.		c.		i.		a.		b.		c.			
Heating	temp.	—	100°	—	100°	—	100°	—	100°	100°	150°	—	100°	—	100°	—	100°
		—	4h.	—	4h.	—	4h.	—	2h.	4h.	12h.	4h.	—	4h.	—	4h.	—
<i>M</i> found	duration	74	104	140	140	148	155	84	84	115	133	129	178	338	320	374	338
<i>NH₂</i> number		0.99	0.67	0.51	0.51	0.43	0.44	0.89	0.88	0.67	0.55	0.55	1.0	0.49	0.50	0.48	0.50
<i>M</i> calc.		73	107	141	141	157	164	81	82	107	131	131	174	355	348	362	348

The observation that the monomer can appear in a second, *insoluble* (and probably unpolymersisable) form (formula IX) alone suggests that

fractions (*b*) and (*c*) consist of a great deal of the *insoluble* monomer with the inclusion of a small quantity of higher polymers. The higher we assume the degree of polymerisation of this component to be, the lower becomes its possible concentration. By far the greater part of the fraction must then consist of the monomer. The general character of the mixture remains in any case a *low-molecular* one.

It is still more probable that no really high polymers are contained in these fractions, and that the mean molecular weight found experimentally coincides roughly with the true molecular weight of the main component of the mixture (this of course does not exclude the possibility of small quantities of trimers or slightly higher polymers being present).

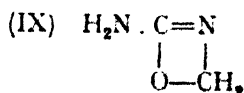
4. Dependence of the Degree of Polymerisation on the Concentration of H-Ions.

Three solutions of **U** and **F**, with $p_H = 1, 3$ and 5 , were used for the preparation of mixtures of polymers (or isomers) of Meth A. These mixtures (*g*) were divided, by *extracting them with hot water*, into a soluble fraction (*k*) and an insoluble one (*i*). From the most acid solution ($p_H = 1$) the insoluble product was obtained almost exclusively. It consisted of the pure (insoluble!) *monomer* Meth A. At $p_H = 3$, the relative quantity of the insoluble residue (*i*) is at its lowest; it consists in equal parts of the dimer and the insoluble monomer. The soluble fraction (*k*)—about 50 per cent. of the total yield—is *monomeric*. At $p_H = 5$ the insoluble residue contains dimer only, the whole of the monomer being soluble. The soluble fraction *k* even contains some soluble dimer (Tables VIII. and IX.).

TABLE VIII.—MOLECULAR WEIGHT CALCULATED FOR MONOMERIC METH A:
 $M = 72$.

p_H	Mixture (g).			Residue (i).				Extract (k).			
	NH ₂ Number.	M Exp.	M Calc. from NH ₂ .	Per Cent. of the Total Mixture.	NH ₂ Number.	M Exp.	M Calc. from NH ₂ .	Per Cent. of the Total Mixture.	NH ₂ Number.	M Exp.	M Calc. from NH ₂ .
1	1.0	93	72	98	0.89	84	81	2	1.1	61	65
3	0.96	84	75	50	0.70	111	91	50	1.0	75	72
5	0.65	115	111	67	0.49	140	147	33	0.76	90	95

There exists thus a *soluble* as well as an *insoluble* modification of the monomeric Meth A; the insoluble one is formed at high p_H -values, and probably has a ring-structure (IX), with one primary NH₂-group.



With decreasing *h* the soluble fraction increases at the expense of the insoluble one. If the work is carried out under these conditions, the amount of the dimer becomes simultaneously increased at the expense of

TABLE IX.

p_H	Mixture <i>g</i> .		Residue (<i>i</i>).			Extract (<i>k</i>).		
	Percentage of the		Percentage of the Mixture (<i>g</i>).			Percentage of the Mixture (<i>g</i>).		
			Found.	Calculated from Molecular Weight :		Found.	Calculated from Molecular Weight :	
				Monomer.	Dimer.		Monomer.	Dimer.
1	~ 100	—	98	82	16	2	~ 2	—
3	82	18	50	23	27	50	~ 50	—
5	40	60	67	—	~ 67	33	25	8

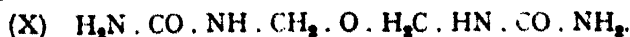
the monomer, because the soluble monomer alone is polymerisable. On the other hand, by simply letting the solutions stand for some time (keeping the p_H -value constant) we should increase the amount of the monomer (which polymerises very slowly at low p_H) and decrease that of the dimer.

By separating the deposit before evaporating the solution, we found—beginning with $p_H 3$ and going to lower h -values—the *second* (polymerising) action of the H-ions. At these low concentrations apparently only very little *insoluble* monomer is formed. The quantity of the primary precipitate (I) (see Table X.) decreases steadily, whereas that of the fraction (Ia), obtained by evaporating the filtrate correspondingly increases.

By extracting with hot water we obtained an insoluble fraction (II) from the precipitate (I); the soluble fraction (IIa) was obtained from the filtrate. With diminishing h not only does the quantity of (I), but also its relative content of insoluble substances (II), become smaller. *The mean molecular weight of (I) decreases therefore to a certain amount with falling h .* The molecular weights of (II) are generally appreciably higher than those of (I), and point sometimes to a trimer. The dissolved part (IIa) contains chiefly the monomer, as does the fraction (Ia), which remained in the initial solution.

5. Analytical Investigation of the Separate Fractions.

The insoluble residue (II) (see Table X.) differs from all the other fractions of Meth A in that its composition differs from the theoretical composition of Meth A (Table XI.). The smaller values found for N and C indicate the formation of a body (X), which contains ether-like oxygen, similar to Meth B. The analytical results can be explained by assuming a mixture of about equimolecular quantities of Meth A and of the compound (X). This compound can be formed together with Meth A, from two molecules of monomethylol urea, but to an appreciable extent only at higher h -values. Since the amount of (X) is mostly very small, the methylene ureas A, which have not been further divided into fractions by extraction, show no appreciable deviation from the theoretical composition $C_2H_4ON_2$, the peculiar resinous fraction (c) not excluded.



Nearly pure Meth B occurs only (as a precipitate) at high h values. If h is less than 10^{-3} , the precipitates have a different composition (Table XI.).

TABLE X.

Mol. weight calculated for Meth A, 72.

Meth B, 174.

Fraction (I) separated after 24 hours.

Substance.	h.	Fraction. ^a					
		I.		Ia.	II.		IIa.
		Per Cent. of (I) + (Ia).	M.	M.	Per Cent. of (I).	M.	M.
Methylene-Urea A.	Exper. series 1†, Meth A.						
	6.3×10^{-3}	81.1	155	71	55.2	214	112
	1.0×10^{-3}	65.8	168	78	29.2	224	99
	1.3×10^{-3}	12.3	143	80	—	—	—
	2.0×10^{-7}	(8.6) *	132	88	—	—	—
	Exper. series 2†, Meth A.						
	6.3×10^{-3}	96.9	122	61	62.3	169	88
	6.3×10^{-4}	90.1	122	62	40.7	174	80
	7.9×10^{-3}	30.5	116	69	27.2	166	75
	2.0×10^{-7}	(72.8) *	115	78	16.1	177	74
Methylene-Urea B.	Exper. series 3, Meth B.						
	6.3×10^{-3}	83.6	173 †	147	100 †	173 †	—
	6.3×10^{-4}	49.6	166	161	85.3	227	108
	7.9×10^{-3}	23.2	145	186	—	—	—
	2.0×10^{-7}	(56.2) *	169	169	21.2	245	147

* Precipitated first after *four weeks'* standing.† Series 1 refers to a more *diluted* formaldehyde solution than series 2; this must explain the differences in the yields.

‡ No soluble fraction could be extracted from (I).

TABLE XI.—(Cf. Table X.)

h.	Methylene-Urea A. Fraction II. (Comp. Table X).				Methylene-Urea B. Fraction I. (Comp. Table X).			
	Per Cent. N.	Per Cent. C from CO.	Per Cent C from CH ₂ O.	Per Cent. C Total.	Per Cent. N.	Per Cent C from CO.	Per Cent. C from CH ₂ O.	Per Cent. C Total.
6.3×10^{-3} .	36.72	16.03	15.69	31.72	32.40	13.63	49.84	33.57
6.3×10^{-4} .	36.85	16.10	15.54	31.60	34.39	14.28	47.46	33.26
7.9×10^{-3} .	36.77	15.97	15.66	31.63	35.88	15.21	47.00	34.01
2.0×10^{-7} .	36.81	16.53	15.51	32.04	30.37	12.24	49.37	31.99
Calculated for Equimolecular Mixture of Meth A + (X).					Calculated for Meth B.			
	36.50	15.80	15.80	31.70	32.2	13.8	51.8	34.5

6. Relation Between Resinous and Non-Resinous Substances.

All the substances obtained by evaporation of the filtrates of Meth B are *resins* of variable composition. The answer to the question, why some fractions of the methylene products are non-resinous and others resinous is probably that resins are formed only from mixtures containing products of different composition. The existence of resins composed exclusively of *pure* polymers or isomers of methylene urea has never been proved, and appears improbable, especially on account of the discovery of a higher oxygenated Meth A fraction (however small this fraction may be). The least amount of an impurity of this kind may suffice to produce a resin. Probably, certain proportions permitting the mutual dissolution of components are especially favourable for this purpose. The relative concentration of the components determines the character of the precipitate, which may be an eutymorphic powder or a mesomorphic resin. The influence of the relative concentrations of the components, depending in its turn upon the conditions of polymerisation, is also revealed by the fact that mesomorphic resins may have both a higher and a lower mean molecular weight, as compared with that of the eutymorphic fractions. Depending on a greater or smaller quantity of the "stabiliser," which permits the insoluble substances to remain dissolved for a longer or shorter time, their polymerisation can attain a more or less high degree. The molecular weight of the resinous fraction (c) of Meth A lies, for instance, between those of the eutymorphic fractions (b) and (d). It may be, that the *monomer*, also, plays the "stabilising" rôle for the polymer (*cf.* p. 389).

The chemical transformations which are necessary for the production of a resin can also be carried out on the already formed Meth B by heating and pressure. It consists in a decrease in the number of CH_2 -groups, and of the primary NH_2 -groups, indicating a polymerisation or condensation (Table XII). The resins obtained in this way are, however, mostly opaque.

TABLE XII.

Found for Meth B.	Per Cent. N from NH_2	Per Cent. N Total.	Per Cent. CH_2O	Per Cent. C from CO.	Per Cent. C Total.
Before pressing	10.19	32.67	50.90	13.70	33.90
After pressing	8.63	29.70	35.86	17.45	32.20

In order to obtain resins with high technical qualities, it is obviously necessary to introduce some higher-molecular components. Transparent resins can be obtained from solutions if the reactions leading, at high *h*-values, to the eutymorphic Meth B are retarded. Reactions giving Meth B at high *h* (for instance $\text{U} + 2\text{F}$, or dimethylol urea in acid solution; or melting dry dimethylol urea) all give resins at lower *h*. The transformation of dimethylol urea into Meth B is a much slower process than the corresponding reaction $\text{U} + 2\text{F}$; it is therefore advisable to use dimethylol urea for the preparation of the resins (F. Pollak's method). The first stage of the condensation is, therefore, carried out in a slightly alkaline solution, and only the second (resinification proper) in a slightly acid medium. A high concentration of H-ions promotes the formation of F from methylol ureas (formation of Meth B from dimethylol urea); this action can be paralysed by strongly increasing the

concentration of formaldehyde. Under these conditions, resins can be obtained even in more strongly acid solutions (John).

In order to accelerate the reaction and to increase the solubility, it is necessary to use *high temperatures* and an optimum concentration of H-ions (with dimethylol urea, about 10^{-4}). Under these conditions, products are formed whose content of "formaldehyde radicals" (methylene, or methylol, or CH_2OCH_2 groups) is greater than that of Meth B. They probably contain *methylol groups*; the stabilising and dissolving action of the latter enables the formation of resins and, possibly, the production of higher polymers (see below). For the resinifying reactions we refer again to the scheme given earlier.

III. Investigation of Complicated Resins.

1. Separation of a Resin-Solution into Fractions (Intermediate Products).

We separated a resin-solution obtained from *dimethylol urea* in slightly acid solution into five fractions (1) to (5). Fraction (1) was deposited spontaneously after long standing; (2) was precipitated from the filtrate by water; (3) was obtained by evaporation of the second filtrate. Fraction (4) we obtained by precipitation with water from the initial solution, and (5) by evaporating the filtrate from (4). In Table XIII. are collected the analytical data obtained with these fractions. We recognise that the fractions (1) and (4), which are deposited from an aqueous solution, have nearly the composition of Meth B, whereas the fractions (3) and (5), which remain dissolved in water, are more similar to methylol methylene-urea (formula (III)); fraction (2) has an intermediate composition. This indicates that the resin is a mixture of substances which are somewhat rich in methylol groups with products containing only few methylol groups or no such groups at all (methylene-ureas). The first are soluble and keep in solution the second, which by themselves are insoluble. By adding water, the concentration of methylol groups is diminished, and the products which are insoluble in pure water precipitated. An opposite effect is observed with highly concentrated *neutral salt solutions*, which have a strongly peptising action.

TABLE XIII.

Fraction.	1.		2.		3.		4.		5.	
Per Cent.	Found.	Calculated for $\text{C}_4\text{H}_{10}\text{O}_2\text{N}_2$ (Meth B) (Form VIII)	Found.	Calculated Equimolecular Mixture Meth B + Methylol Methylene-Urea (III)	Found	Calculated $\text{C}_4\text{H}_8\text{O}_2\text{N}_2$ (Methylol Methylene-Urea III).	Found.	Calculated $\text{C}_4\text{H}_{10}\text{O}_2\text{N}_2$ (Meth. B VIII.).	Found.	Calculated $\text{C}_4\text{H}_8\text{O}_2\text{N}_2$ (III).
C .	34.78	34.46	35.24	34.86	36.08	35.27	35.26	34.46	35.76	35.27
H .	5.82	5.79	5.82	5.86	6.05	5.93	6.15	5.79	5.85	5.93
N .	31.29	32.18	30.27	29.81	28.56	27.45	31.81	32.18	28.24	27.45

Protective Action.—The above-described experiments show—in accordance with the results obtained with methylene-ureas (see earlier), that resins (at least the intermediate products) contain components which

act as "stabilisers" or "protective colloids" in respect to some other of their components. The "protective" substance is formed simultaneously with the other components. In the case in question, the protective action is obviously due to the methylol compounds; the methylol group CH_2OH acts as a "lyocratic" group.

The protective action not only stabilises the simultaneously formed insoluble methylene compounds, but increases the polymerisation capacity of the protective substance itself as well. The above-mentioned methylol methylene urea (III) can, for instance, polymerise to the compound (XI), and this latter in its turn to ring-systems of the kind (XII) (see below).

The stabilising action of the "protectors" obviously favours the formation of higher polymers, which would otherwise separate from the reacting mixture.

High h -values cause a decomposition with loss of CH_2O and formation of Meth B, and thus prevent the formation of protective bodies; low h -values slow down the reaction. Therefore, optimum concentration of H-ions must be maintained, and the reaction must be supported by heating.

2. Investigation of the Resinification Reaction.

Determination of the Water Formed by Condensation.—Meth B is formed from dry dimethylol urea by heating it, for a long time, above its melting-point. The melted mass becomes acid during the reaction (formation of formic acid). It was found* (Walter) that by decreasing h (i.e., by adding alkaline substances) we obtain *resins* instead of Meth B. Water (and some formaldehyde) are formed during the process. Quantitative analysis showed—as a mean value—the production of 1.4 mol. water and 0.2 mol. formaldehyde per urea radical. By melting pure dimethylol urea (without alkaline substances) we obtain 1 mol. H_2O and 0.5 mol. formaldehyde, in accordance with the formula of Meth B (Table XIV). Melting of monomethylol urea gives Meth A under all conditions. From the " H_2O -number" 1.4 we may conclude that,

TABLE XIV.

	Dimethylol Urea.					Monomethylol Urea.			
	Pure.	Different Additions.			Calc. for Meth B.	Pure.	With Additions		Calc. for Meth A.
		1	2	3			1	2	
Mols. per urea-radical									
Of H_2O	1.00	1.39	1.44	1.38	1.00	1.0	0.96	0.96	1.0
Of CH_2O	0.50	0.24	0.17	0.15	0.50	0.0	0.08	0.03	0.0
Methylene- and methylol-groups together	2	1.79	1.60	1.79	1.5	0.99	0.94	1.02	1.0

in addition to open chains (as in (XI)), whose H_2O -number cannot exceed 1.0, some "ring-chains" (for instance of the kind (XII), or its isomers) or more complicated ring-systems (e.g. (XIII)) are also formed; the H_2O -number of the latter substances may be as high as 2.0. (XI) can be

* D.R.P., 512, 566; Chem. Centr., 1928, 2, 1383, 1498.

TABLE XV.

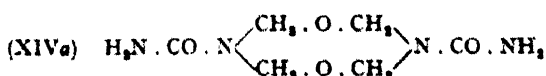
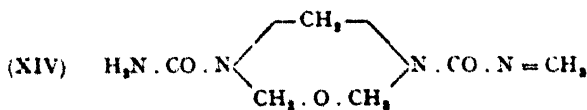
Substance.	Urea.	CH ₂ Urea.	(CH ₂) ₂ Urea Asymm.	(CH ₂) ₂ Urea Symm.	Mono-methylol Urea.	Dimethylol Urea.	Meth A, Monom.	Meth B.	Resin 1.	Resin 2.	Resin 3.
Number of metal atoms absorbed per urea-radical .	1 and 2	1	1	0	1 and 2	1 and 2	1	0.5	about 0.5	about 0.5	about 0.5

Determination of the Primary NH₂ Groups in Different Stages of the Resinification Process.—The determination of the number of primary NH₂ groups in the resins in question does not give so definite a clue to the nature and number of the end groups, as is possible in the case of the methylene-ureas A and B. The formation of formaldehyde (as described above) and the analytical determination of CH₂ groups both showed that the end product does not contain much less than 2 formaldehyde radicals (methylene and methylol groups) per urea-radical (thus corresponding, e.g., to the schemes (XI) to (XIII)); consequently, practically no primary NH₂ groups will be present. In determining the amido-groups in three fractions of resins, corresponding to subsequent stages of condensation of dimethylol urea, we unexpectedly found that in the initial stages (II) and (III), a large number of primary NH₂ groups were present, although there were no such groups in the dimethylol-urea (I) itself (Table XVI).

TABLE XVI.

Substance.	Stage of Condensation.	Per Cent. N from NH ₂ .	Per Cent. N Total.	Per Cent. CH ₂ O.	Per Cent. C from CO.	Per Cent. C Total.	Mol. Weight Found.
Resin No. 1	(I) Dimethylol-urea)	0.0	23.3	50.0	9.9	30.0	—
	(II)	8.2	24.1	49.8	10.1	30.0	—
	(III)	7.0	25.2	50.5	10.8	31.2	—
	(IV)	0.0	29.2	51.9	11.9	32.7	—
Meth B	—	(10.1)	32.2	51.8	13.8	34.5	—
Dimethylene-urea	—	(0.0)	33.3	71.5	14.3	42.9	—
Resin No. 2	—	0.0	30.2	52.3	12.2	33.5	400
Resin No. 3	—	0.0	20.0	53.3	13.2	34.4	—

This result can be explained by assuming some components of the resin-mixture to have structures of the kind (X) or of the kind of Meth B, with ether-like oxygen (formula (XIV)).



The resin-forming process leads further to a disappearance of the NH₂-groups, probably by linking (XIV) with other methylene, or

methylol compounds; the fraction (IV) in Table XVI., which corresponds to the end-product, and also the resins Nos. 2 and 3, contained no longer primary NH_2 -groups.

A direct determination of the molecular weight of resin No. 2 in formic acid gave only 400 as average value (Table XVI.). This relatively low result, which corresponds to a mean order of polymerisation not higher than about 5, does not exclude the existence of a certain proportion of much higher polymers. The products of higher technical value, which probably contain more highly polymerised components, are generally insoluble (without decomposition) in formic acid and in any other solvent. It is therefore impossible directly to determine their molecular weight. Formic acid is the only solvent which dissolves at least the low-molecular resins apparently by forming formates.

Composition and Structure of the Resins.—The above-described results show that these resins are much more complicated in structure than those which consist chiefly of polymers or isomers of Meth A or Meth B. They are mixtures of compounds containing little with compounds containing much oxygen; the latter probably include the groups $\text{CH}_2 \cdot \text{O} \cdot \text{CH}_2$ or CH_2OH ; they may also contain tightly bound H_2O . Table XVI. shows the analytical composition of a number of such resins, in nearly the "final" state. Other resins have, however, a different composition; the only general rule is that the composition lies between that of dimethyl urea and that of Meth B and/or dimethylene urea. From the data corresponding to the stages (I) to (IV) in Table XVI. one sees that (II) still has the composition, but not the structure, of the initial dimethylol urea; in (III) and (IV) the N- and C-values became gradually higher, so that the composition of (IV) only slightly differs from that of Meth B. The resemblance is, however, only superficial; the determination of the water and formaldehyde losses during condensation indicate that, in the resins, the content of formaldehyde-radicals must be much higher, and the polymerisation must have proceeded much further than in Meth B. The increase of N and C is obviously due to the greater loss of water and smaller loss of formaldehyde than to the formation of Meth B.

With progressing formation of resin, the substance gradually loses its methylol groups (which have by now fulfilled their protective action), for instance by rings-formation from several molecules (XI). The most important components of the final, insoluble and infusible product are *polymeric dimethylene ureas*. The product contains, however, all kinds of their isomers, more highly oxygenated substances (e.g. XI or XIV) and other related compounds, as well as Meth A and Meth B.

The occurrence of *ring-systems* in resins is proved; open chains can form (if they are present at all) only a part of the resinous mixture, stabilised by them as a solid solution. It can be supposed that not only one-dimensional "ring-chains" of the kind (XII), but also net-like compounds (e.g., XIII) are formed in the course of condensation and present in the final product, especially in the technically important resins.

As to the *size of the molecules*, it was proved that *some F.U. resins* have a relatively low molecular weight. In spite of their low degree of polymerisation the pure methylene ureas (the monomere too!) as well as the resins are infusible and only slight, if at all, soluble in water. The formation of ionic complexes or micelles in acid solution (see the paper "Ionic Complexes of Polymeric Compounds") indicate

that, in the solid products also, the lowly polymerised components are united to micelles. *By the formation of micelles and/or ring-systems the products obtain the character of insoluble and infusible substances.* Of course, it is also possible that certain U.F. resins attain a higher mean degree of polymerisation which, however, has not been proved.

IV. Observations as to the Reaction Mechanism.

The later a fraction of methylene ureas is deposited spontaneously from the solution, the higher is, generally, the average molecular weight of the precipitate (*cf.* fractions (a) to (d) in Table V.). These results indicate that the polymerisation proceeds *by stages*.

Formation of Ions in Acid Solution of Methylene Compounds.

—By adding sodium hydroxide to a clear aqueous solution of the methylene-compounds the latter are *at once* precipitated from the solution; only in slightly acid solutions do they remain dissolved for some time. (Under ordinary conditions the solution is always slightly acid, due to the formation of formic acid from formaldehyde.) This indicates the formation of small quantities of *formates* from methylene urea and formic acid; on addition of alkali the unstable base is freed and decomposes quickly with precipitation of Meth A or Meth B. This assumption involves the maintenance in solution of a large number of insoluble neutral molecules, bound to a complex by one single ionogenic molecule. This is what actually occurs, according to Wo. Pauli, with the so-called "electrocratic" colloids. We intend to investigate this question more closely, although the instability of the solutions makes it rather difficult.

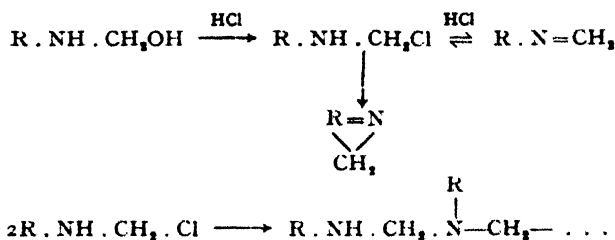
Quite different are the relations in the case of *resin-solutions* (prepared, for instance, from dimethylol urea). They are *stabilised* in alkaline solutions. The methylene ureas have obviously an electro-positive character; this assumption agrees well with the formation of formates in absolute formic acid, proved by measurements of electric conductivity. The resins appear to be amphoteric compounds, because acid methylol-groups are present in their molecules. During the resinisation-reaction, the negative methylol ureas are gradually transformed, with loss of methylol groups, first into an amphoteric intermediate form (resins), then into an electro-positive methylene derivative. The resins occupy thus an intermediate position between the methylol and the methylene-compounds, not only in relation to the conditions of their formation and their composition, but also in their electrochemical properties.

The rôle played by the acid in the polymerisation-process seems, however, to be based on a linking different from that in the formates. In studying the change of the concentration of H-ions during the polymerisation of dimethylol urea we found indications of the acid being bound by the reacting substances. The measurements are not very reliable, because of the inhomogeneities occurring in the mixture. The *h*-values are found to decrease in the first stage of condensation, but later to increase again, and finally to approach their initial magnitude. The increase of *h* in the later stage is probably due not to the original acid being set free again, but rather to the formation of fresh formic acid from formaldehyde (Table XVII.). The minimum of *h* corresponds to the longest time the solution remains clear; *before* this point amorphous, *after* that resinous deposits are precipitated on cooling.

TABLE XVII.—VALUES OF $h \times 10^3$.

Condensation: Duration in Minutes.	0.	5.	10.	30.	40.	50.	60.	110.	150.	190.
Series 1	2.1	1.6	2.0	---	---	---	---	---	---	---
" 2	7.1	---	---	1.5	1.0	2.3	7.0	---	---	---
" 3	0.35							0.16	0.37	0.36

Following A. E. Dixon, we may assume the acid to be bound in a way similar to that in which it is bound in the esters. In this case, the scheme of polymerisation would be as follows :



If the acid is freed *intramolecularly*, we obtain the monomeric (soluble or insoluble) form ; if it is freed *intermolecularly*, we get polymers. The actual direction of the process depends on the initial h -value. The polymerisation by heating of the dry methylene ureas can also probably proceed without the catalytic action of an acid (formic acid).

Summary.

The U.F.-resins contain generally components of different composition, structure and molecular weight. Their mode of formation, and their composition are both intermediate between those of the easily soluble, crystalline *methylol* compounds and of the nearly insoluble, amorphous powders of the *methylene* compounds of urea. We first describe the properties of the methylene-ureas $\text{C}_2\text{H}_4\text{ON}_2$ (Meth A) and the higher oxygenated $\text{C}_6\text{H}_{10}\text{O}_2\text{N}_4$ (Meth B), and study the properties of the complicated resins themselves.

With *methylene-compounds*, we have determined the molecular weight (in formic acid), and the primary amido-groups (as end-groups) : both methods gave identical results as to the molecular size. For the determination of the elementary composition a simple method was evolved, which is based on heating with magnesium-chloride. The dissolution of the methylene-compounds in formic acid was found to be accompanied by formation of ionic complexes or micelles.

By fractionation, we separated a *monomer*. Further fractions contained polymers, but with a comparatively low average molecular weight (dimers or trimers). These fractions are not mixtures of the monomer with more highly polymerised substances. The last fractions, which are insoluble in formic acid, contain trimers.

The high specific viscosities in formic acid are similar to those of all other urea-derivatives, and are probably influenced chiefly by the complexity of ions.

Formulae are proposed for the constitution of the compounds, Meth A and Meth B. The monomer contains one, the dimer $\frac{1}{2}$ NH_2 -group per urea-radical.

Meth A exists in two forms, soluble and the insoluble; the latter probably has a ring-structure, and is the main product at higher concentrations of the H-ions ($p_H = 1$).

The *methylene-compounds* appear not only as "euthymorphic" powders, but also as "mesomorphic" resins. By fractionating Meth A we have been able to obtain a small fraction having the composition of pure Meth A and the molecular weight of a dimer, with the properties of a resin. Of the fractions of Meth B, the last is always resinous. One fraction of Meth A contains—usually to a very small extent—a different compound, with more oxygen, being probably bound in an ether-like manner. The methylene-urea prepared by the ordinary method is therefore not completely homogeneous. Similar results were obtained with Meth B.

With decreasing concentration of H-ions the yield of euthymorphic methylene-urea deposits becomes smaller. If the proportion 1U per 2F is maintained, resins appear instead. All reactions leading to Meth B at high H-ion-concentrations, yield resins under conditions which slow the reaction down; these are more complicated than those formed from Meth A or Meth B.

By fractionating them, we obtained soluble fractions, which contain more oxygen (methylol groups), and insoluble fractions with less oxygen. The former act as "stabilisers" or "protective colloids," keeping the latter in solution. Dilution with water counteracts the protective action and precipitates the insoluble components of the mixture. An opposite effect is caused by concentrated saline solutions.

The determination of water lost during the condensation indicates the formation of ring-systems. From the amount of alkaline metals absorbed it is concluded that one methylol group (or one mol. of tightly bound water) is present per two urea radical.

In the course of resinification of dimethylol-urea, the resin becomes poorer in oxygen and approaches the composition of a polymeric dimethylene-urea. The composition of the end product lies midway between those of dimethylol urea and of Meth B and/or dimethylene-urea.

The linking of the monomeric molecules either correspond to true polymerisation or involves condensation as well.

The precipitation of the methylene-compounds by alkalis indicates the existence of ionic complexes determined directly by another method.

The methylol group possessing properties of a weak acid, the resins with properties intermediate between those of methylene and of methylol-ureas, can be generally expected to be amphoteric.

The polymerisation appears to proceed in steps. Acid disappears at the beginning of the process, and reappears to the end of it.

In spite of their low degree of polymerisation the products, by the formation of micelles and/or ring-systems, attain the character of insoluble and infusible substances. Of course, it is also possible that certain U.F. resins attain a higher mean degree of polymerisation, but this has not been proved.

IONIC COMPLEXES OF POLYMERIC COMPOUNDS.

BY GEORG WALTER, *Vienna.*

Received in German the 9th September, 1935.

Translated by Dr. E. Rabinowitsch.

During the investigation of the urea-formaldehyde condensation (described in the foregoing paper) we established the structures and determined the molecular weights of two methylene-derivatives of urea, $C_2H_4ON_2$ ("Meth A") and $C_2H_4O_2N_2$ ("Meth B"), especially of the first one. By determining the primary NH_2 -groups (by means of nitrous acid), and by measuring the molecular weight (using both the cryoscopic method and that of Barger-Rast) we found that Meth A and Meth B both form *polymers*, containing primary NH_2 -groups on one end of the molecule. We therefore proposed the following formulæ for the three polymeric forms of Meth A:

I. $H_2N \cdot CO \cdot N = CH_2$. II. $H_2N \cdot CO \cdot NH \cdot CH_2 \cdot HN \cdot CO \cdot N = CH_2$.
 III. $H_2N \cdot CO \cdot NH \cdot CH_2 \cdot HN \cdot CO \cdot NH \cdot CH_2 \cdot HN \cdot CO \cdot N = CH_2$.

TABLE I.

Fraction.	λ .	α .	% N.	P_1 from NH_2 .	P_2 from Mol. Weight.	K_1 .	K_2 .	$P_2 =$ $K_1 \cdot P_1$.	$K_2 P_1$.
Methyleneurea "A".									
1	9.23	0.155	19.33	1.01	1.03	1.5	1.31	1.5	1.3
2	9.60	0.160	16.41	1.18	1.16	1.6	1.4	1.9	1.6
3	9.96	0.165	16.30	1.19	1.17	1.7	1.4	2.0	1.7
4	9.65	0.160	13.10	1.49	1.45	1.9	1.5	2.9	2.2
5	10.35	0.172	12.39	1.57	1.60	2.2	1.5	3.4	2.4
6	10.90	0.180	10.19	1.91	1.85	3.3	1.7	6.0	3.2
7	9.71	0.160	9.94	1.96	1.95	2.7	1.6	5.4	3.2
8	9.95	0.165	9.23	2.11	1.95	3.3	1.7	7.1	3.6
9	10.10	0.168	8.42	2.31	2.06	4.5	1.8	10	4.1
10	10.30	0.172	8.42	2.31	2.16	4.9	1.8	11	4.2
Methyleneurea "B".									
11	5.38	0.090	15.90	1.01	1.02	1.6	1.4	1.6	1.4
12	5.73	0.095	8.30	1.94	1.84	3.9	1.7	7.5	3.4
13	6.18	0.103	8.00	2.02	1.94	5.9	1.8	12	3.7
14	6.19	0.103	7.90	2.08	1.94	6.0	1.9	13	3.8
15	6.23	0.104	7.69	2.10	2.14	7.7	1.9	16	3.9
16	6.25	0.104	7.25	2.22	2.24	13.6	1.9	29	4.3

Table I. shows that the degrees of polymerisation P_1 , calculated from the determination of NH_2 -groups, agree well with those, P_2 , found by direct measurement of the molecular weight of Meth A dissolved in absolute formic acid. A large number of fractions (only a part of which are included in Table I.) were prepared either by spontaneous deposition, by polymerisation by heat, or by extraction with hot water. Table I. shows that the degree of polymerisation of all these products is somewhat low. The trimer is seldom attained; most fractions give values lying between those of the monomer and the dimer. It was possible to prepare the monomer and the dimer, although probably not yet in a perfectly pure state.

Despite the practical identity of the molecular weights calculated from the NH_2 determination with those found by direct measurement, the results became somewhat doubtful when it was discovered that solutions of methylene-urea in formic acid have a marked electric conductivity. This must be due to the formation of salts (formates). In Fig. 1 the conductivities are plotted against the square root of concentration for urea itself and for a number of its derivatives, containing one or several methyl-, phenyl-, or methylol-groups. The concentrations are expressed by the number of mols of urea-radicals per litre. The methylol compounds are related genetically to the methylene ureas, the four curves in Fig. 1 illustrate the electrolytic behaviour of the last substances in monomeric and dimeric form.

Fig. 1 clearly shows the influence of the substituents upon the conductivity.

The following rules hold: "positive" groups (e.g. methyl) increase the conductivity (as compared with that of urea itself); "negative" substituents decrease it. A second substituent of the same sign enhances the action of the first; substituents with different signs mutually weaken their influence. Methylene and methylol are both "negative" substituents, thus resembling phenyl. Methylol ($-\text{CH}_2\text{OH}$) has the strongest influence; methylene (in the form of $-\text{N}:\text{CH}_2$ or $-\text{HN}:\text{CH}_2-\text{NH}-$) comes next, phenyl last. The position held by methylol in this series is due to its slightly acid character. An analogous explanation must be given for the fact that the Meth B-curves lie generally below those of Meth A: the first compound contains relatively more oxygen, probably because of the occurrence of a CH_2OCH_2 group (or of a CH_2OH -group) in its molecule. The higher conductivity of the dimers as compared with the monomers will be discussed below.¹

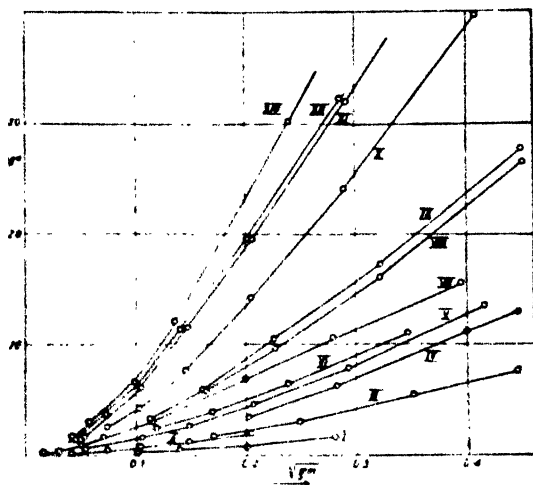


FIG. 1.

- | | |
|----------------------------|----------------------------|
| 1. Triphenyl Urea | 8. Methylene Urea, "A." a. |
| 2. Sym. Diphenyl Urea. | 9. Methylene Urea, "A." c. |
| 3. Dimethylol Urea | 10. Urea. |
| 4. Monomethylol Urea. | 11. Methyl Urea |
| 5. Methylene Urea, "B." a. | 12. Sym. Dimethyl Urea. |
| 6. Methylene Urea, "B." c. | 13. Tetramethyl Urea. |
| 7. Phenyl Urea. | |

¹ The monomer is marked a, the dimer with c.

In the second column of Table I., are collected the equivalent conductivities λ of the single fractions of Meth A. The numbers given are those found for 0.1 *N* solutions (urea radicals being treated as divalent). From these data, we may calculate the corrections which must be applied to the values P_2 or P_1 , in order to take account of the electrolytical dissociation (the degree of dissociation α is about 15 per cent. at this concentration.²) In the case of polymerising ions, even a relatively small dissociation may cause an important correction, which becomes greater with increasing P_1 . Table I. shows that the re-calculated (apparent) degree of polymerisation

$P_2 = \frac{P_1}{1 - 2\alpha P_1}$ is 1.5 instead of 1 in the case of the "monomer" of Meth A (exp. 1), and as much as 6 (instead of 2) in the case of the "dimer" of the same substance (exps. 7 and 8).³

If the newly calculated polymerisation-degrees P_2 were to be considered as the real ones, then the NH_2 -determination must be wrong and the accordance of its results with those of the direct measurement of molecular weight a pure coincidence. Two arguments support the assumption that this is not the case: (1) The observation that the above-mentioned coincidence occurs in *all* cases; and (2) The fact that the NH_2 -method was found to give satisfactory results in the case of the methylol compounds of urea, which, although related to the methylene-compounds, are much less stable than the latter. No danger exists, therefore, of error due to decomposition of Meth A and formation of formaldehyde during the measurements.⁴ The degrees of polymerisation P_1 obtained by the NH_2 method (identical with the values P_2) must therefore be explained in a different way. The explanation may be the formation of *ionic complexes*. The complexes must be ions, and not associations of neutral molecules, because only the assumption of complex ions can reconcile the degrees of polymerisations P_1 and P_2 with the conductivity measurements. We must assume that the formation of complexes counterbalances exactly the increase in the number of particles due to electrolytic dissociation.

If the particles linked in this way to the original ions are themselves ionised, then the degree of complexity K_1 (which is only a mean value, like the degree of polymerisation P) can be calculated by means of the formula

$$K_1 = \frac{P_2}{P_1} = \frac{1}{1 - 2\alpha P_1}$$

(or, for Meth B, $K_1 = 1/(1 - 4\alpha P_1)$). For the dimers of Meth A (exps. 7 and 8), K_1 is in the neighbourhood of 3, for the dimers of Meth B (exp. 13) it is about 6. On the other hand, we may assume the particles linked to the primary ion in the complex to be neutral molecules. In this case, the degree of complexity would be $K_1 = 1 + 2\alpha P_1$. The values K_1 are generally smaller than K_2 . Moreover, they increase with increasing P_1 . For the dimer of Meth A, K_1 is approximately 2 (Table I.). By multiplication of K_1 (or K_2) by P_1 , we obtain the number of urea radicals in one (polyvalent) ion—a number including both the degree of polymerisation and the degree of complexity.

In making the calculations, we assumed the ions to have either the valency $2P_1K_1$ or (in the case of neutral partners forming the complex) the valency $2P_1$. We further assumed the value $\lambda_\infty = 60$, which was found experimentally for other formates dissolved in formic acid. We disregarded the diminution of the λ_∞ -value which may be due to the greater

² The molecular weights were determined at this same concentration; they change, however, only very slightly with concentration. The value of α was calculated by putting $\lambda_\infty = 60$ (see further below).

³ Meth A is taken as divalent; the corresponding equation for the tetra-valent Meth B is $P_2 = P_1/(1 - 4\alpha P_1)$. The numbers found for the monomeric and the dimeric fraction are printed in italics in Table I.

⁴ A decomposition of this kind could produce new NH_2 -end groups; in this case the P_1 -values found would be too small.

size of the particles, caused by polymerisation as well as by formation of complexes. As shown by Fig. 2, the equivalent conductivities λ of the methylene ureas increase slowly even at the highest dilutions; it is therefore impossible to determine λ_{∞} by graphical extrapolation.

This slow increase of λ and of α , as well as the small absolute values of these magnitudes, must be due to the presence of complexes, which are well known to cause phenomena of this kind. In Table I. we gave the equivalent conductivities λ (calculated for 1 mol. urea-radicals per 2 litres) for 0.1 *N* solutions of different methylene urea fractions. By assuming monovalency of the monomer, and calculating the equivalent conductivity for 1 urea-radical per litre ($\lambda_{gm.}$), (still using the value 60 for λ_{∞}) we still obtain numbers which are much smaller than these found, for instance, for sodium formate in formic acid. Table II. shows that sodium formate is almost completely dissociated already at a dilution $v = 4.9$. In the case of the monomer Meth A, however, this dilution corresponds to a degree of dissociation of not more than 20 per cent. (not more than 10 per cent., if we assume divalency and $\lambda_{\infty} = 60$, giving together $\mu_{\infty} = 120$). In Fig. 2 the conductivities $\lambda_{gm.}$ (calculated for 1 mol of urea per litre, irrespective of the degree of polymerisation) are plotted against the square root of the concentration. We recognise a slow increase of $\lambda_{gm.}$, which continues even at the lowest concentrations, thus pointing towards a gradual "activation" of all possible valencies of the molecule.

This behaviour suggests that the particles which lead to the formation of the complex ion are neutral molecules; it is therefore probable

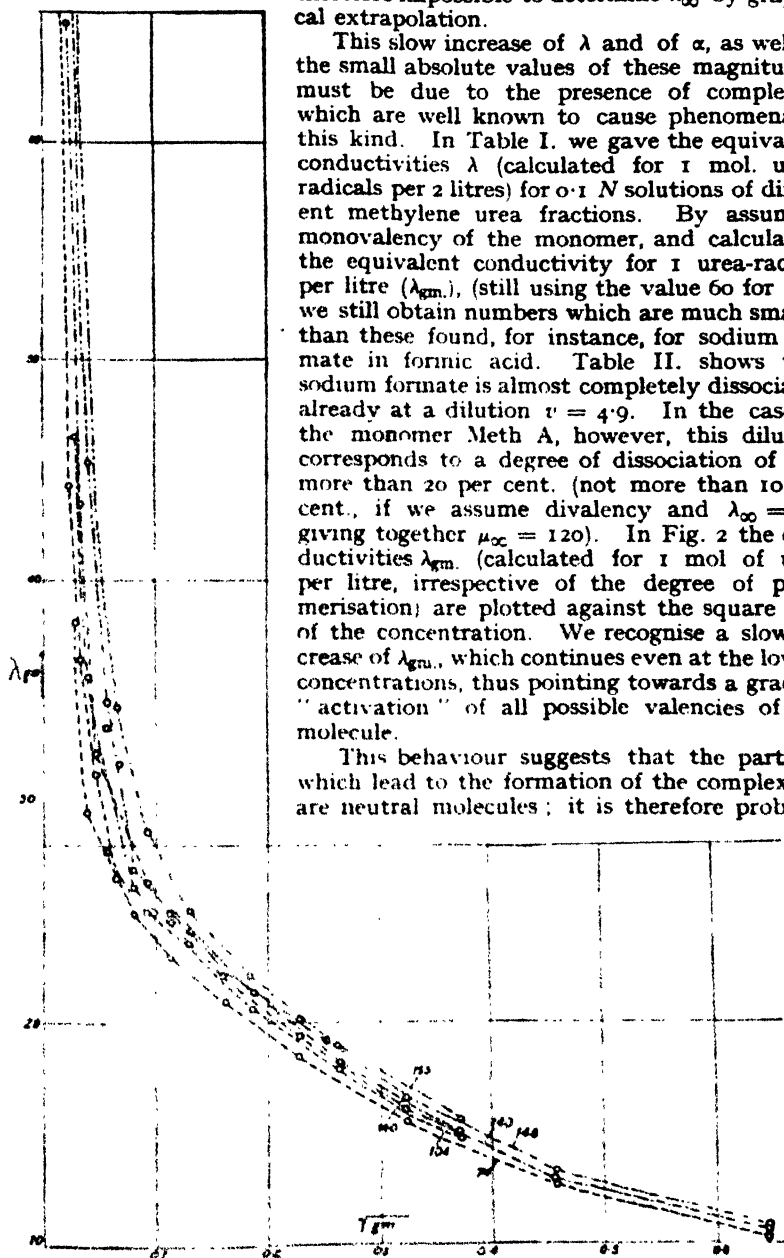


FIG. 2.

that the smaller K_1 values have a more real meaning than the K_2 values. It is, however, to be kept in mind, that the K_1 values also increase with increasing degree of polymerisation; in cases of high polymerisation (although

not in the one we are now concerned with) they may obtain quite considerable values.

TABLE II.

Meth A monomer.

ν	2.4	4.8	9.6	19.2	38.4	76.8	153	306	612	1224
$\lambda_{gm.}$	10.3	12.7	15.6	18.5	21.0	23.0	24.9	27.7	29.5	38.0

NaCOOH.

ν	4.9	11.4	22.8	24.0	32.0	45.7	47.0	∞		
$\lambda_{gm.}$	54.2	59.6	62.2	50.7*	58.0*	63.1*	60.0*	66		

* Measurements by Hantzsch. Other data are by Schlesinger and Martin; taken from P. Walden, *Das Leitvermögen der Lösungen*, II., 218 (1924), Leipzig.

Fig. 2 shows further that the equivalent conductivity generally increases with the molecular weight and degree of polymerisation P_1 . On Fig. 2 are indicated the corresponding molecular weights; the upper curves are those with the highest molecular weights. It is not improbable, that this increase is due—at least partially—to the changes in the substitution of NH_2 -groups which are concerned with polymerisation (the combination

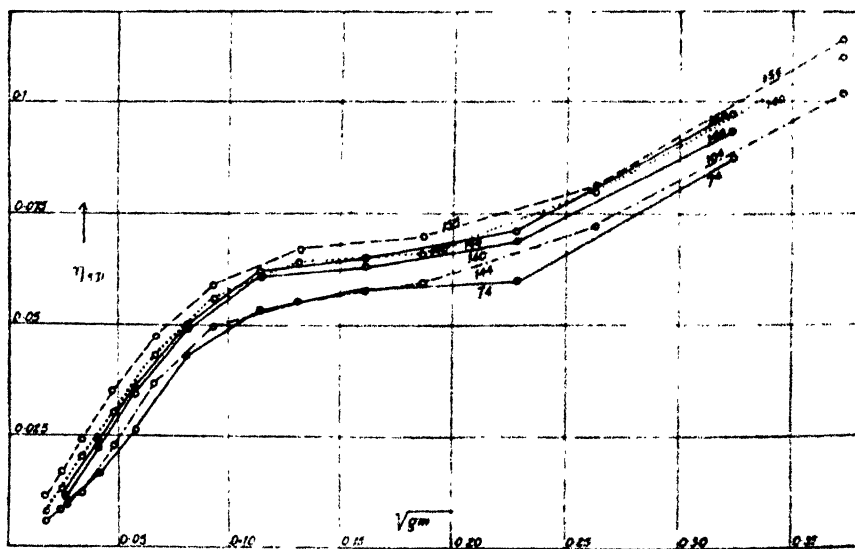


FIG. 3.

$H_2N + N : CH_2$ being transformed into $HN \cdot CH_2 \cdot NH$; see above). An analogous connection exists between the specific viscosity and the degree of polymerisation (Fig. 3). The parallelity between the specific viscosity and the equivalent conductivity, as well as the high absolute values of the former, may be connected with the complexity of the ions. The viscosity is of the same order as that of the others (non-polymerising) derivatives of urea (cf. this vol., p. 383, Table VI.).

The shape of the curves showing equivalent conductivity as a function of dilution is, however, somewhat different in the case of urea (or the methylene ureas) and that of the methylene ureas. Fig. 4 shows that the curve for urea approaches a constant limit which is not very different from $\lambda_{\infty} = 60$. Since the concentrations are measured by the number of urea-molecules per litre, this result indicates the monovalency of urea ions, since the value $\lambda_{\infty} = 60$ was found for monovalent ions. (Our previous arguments are, however, not changed in principle by the assumption of monovalency. The values of α are to be doubled, and the equation for K_2 becomes $K_2 = 1 + \alpha P_1$). Symmetrical diphenyl-urea and symmetrical dimethyl diphenyl-urea show some resemblance with the methylene-ureas inasmuch as their λ_{gm} -values are relatively much smaller.*

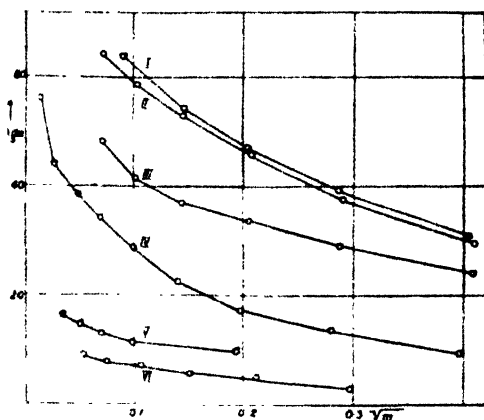
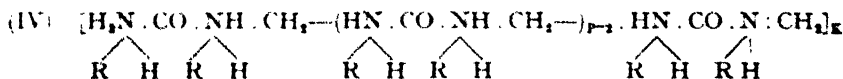


FIG. 4.

- I. Sym. Dimethyl Urea.
- II. Methyl Urea.
- III. Urea.
- IV. Phenyl Urea.
- V. Sym. Dimethyl Diphenyl Urea.
- VI. Sym. Diphenyl Urea.

The average structure of the methylene-urea complexes is illustrated by formula (IV). (The free charges are not shown.) P_1 indicates the degree of polymerisation, K_1 the degree of complexity, and R an acid radical.



The methylene-compounds of urea are closely connected with the urea formaldehyde resins (*cf.* this vol., p. 377). Since the polymerisations leading to the formation of resins are also catalysed by acids (usually by formic acid), it is not impossible that ionic complexes may play a rôle in this process, in which higher polymers are surely involved. Already, with $P_1 = 5$, we obtain from $K_1 = 1 + 2\alpha P_1$, $K_1 P_1 = 55$ (at this high dilution, α must be equal to 1). The formation of complex ions cannot change the mean degree of polymerisation, the quantity of acid present being very small in comparison with that of urea. It would seem possible that the acid may catalyse not only the ordinary polymerisation process, but also the formation of complexes, in the following way: First, the acid ion associates itself with a neutral molecule; this charged system attracts more molecules and a complex ion is formed. Finally, the acid ion leaves the complex (if only to associate itself with some other particles). The remaining neutral complex may hold together, even after the loss of the charge.

Summary.

The comparison of electrical conductivities of monomeric and polymeric methylene-ureas in formic acid with the results of the direct determination

* Meanwhile it has been stated that all ureas, too, form complex ions in formic acid, also to an extent that the influence of electrolytic dissociation is counterbalanced.

of the molecular weights in the same solvent, as well as with those of the determination of primary NH_2 -end-groups shows that ionic complexes must be present in these solutions.

In the formation of complexes the increase in the number of particles due to electrolytical dissociation is always exactly counterbalanced by the decrease due to the production of complexes. Direct determinations of molecular weight give therefore results which show no signs of electrolytical dissociation. Only from the results of all three methods together—determination of the end-groups, conductivity and molecular weight—is it possible to show the formation of complexes. The equivalent conductivity varies with the degree of polymerisation and with the nature of the substituents in the amido group. The influence of positive and negative substituents has been examined. In formic acid all ureas give complex ions.

The degree of complexity increases with growing polymerisation. The complexity can, however, obtain remarkable values even at very low polymerisations under certain conditions.

The formation of complex ions makes the equivalent conductivity of the methylene urea formates appear low as compared with that of other formates.

As a hypothesis, it is suggested that in the formation of *resins* from urea and formaldehyde the formation of ionic complexes or micelles (in slightly acid solution) plays a certain rôle additional to ordinary polymerisations.

CONDITIONS UNDER WHICH INSOLUBLE AND INFUSIBLE RESINS ARE PRODUCED, ESPECIALLY THOSE FORMED BY ARYL-SULPHAMIDE AND FORMALDEHYDE.

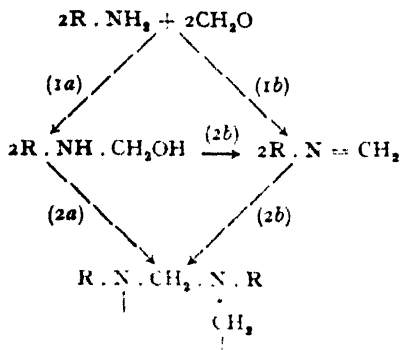
BY GEORG WALTER, *Vienna*.

*Received in German, 9th September, 1935, and translated by
Dr. E. Rabinowitch.*

The aryl-sulphamides offer a very convenient example for the investigation of the conditions under which soluble or insoluble, fusible or infusible resins are produced. By simply changing the number and/or the nature of the substituents (SO_2NH_2) in the benzene ring it is possible to change the properties of the resins formed by condensation of the sulphamide with formaldehyde. This problem, moreover, has a technical interest: resins which, by continued polymerisation or condensation, finally become insoluble and infusible (a process known as "hardening") are of special technical importance. Important examples are the so-called phenoplasts and aminoplasts. The latter include the urea formaldehyde resins.

The condensation of phenols or amides with formaldehyde can be considered as a two-stage process. (1) The *primary condensation* of phenol or amide with aldehyde, giving a "primary condensation product," and (2) the further condensation or polymerisation of the primary product. Process (1) leads to the formation of a product containing methylol groups (CH_2OH). (These groups substitute for instance an H-atom in the benzene ring of phenol or in the NH_2 group of the amide). The methylol group can bring about further polymerisation in two ways: either by intermolecular dehydration, as in (2a), or by intramolecular loss of water, followed by a combination of two dehydrated molecules

—as in (2b). Both may lead to the formation of one and the same condensation product:



In order to link together more than two molecules, the basic molecule (phenol or amide) must contain at least two active-atoms. In the case of phenol, aromatic H atoms in appropriate position in the ring may play this rôle; in the case of the amides, those of the NH_2 -group.¹ To enable the formation of a doubly bound methylene group, as in (2b), the two reacting H atoms must be near each other.

Until recently, only soluble and fusible resins were known belonging to the aryl sulphamide class. They were obtained, for instance, by condensation of *p*-toluene sulphamide with formaldehyde. We found that by introduction into the molecule of a second group capable of reacting with formaldehyde, e.g., another SO_2NH_2 , or $CONH_2$, or simply NH_2 , it is possible to obtain *insoluble* and *infusible* resins, which can be hardened.

Products of this kind were prepared for instance from *m*-benzene di-sulphamide, from 1, 3, 5-benzene trisulphamide, from *meta*- and *para*-sulphamide benzamide, from the aniline sulphamides, etc. Analogous results were obtained in the series of naphthalene sulphamides: The mono-sulphamides produced soluble, the di- and tri-sulphamides insoluble resins.²

These experiments lead us to the general conclusion,³ that in order to obtain hardened resins, it is necessary to use substances with more than one active group in the molecule.

Exceptions to this rule (i.e., cases in which, despite the presence of two active groups, no insoluble resins can be obtained) occur either when one of the two groups does not react with aldehyde, or when the product of this primary reaction is in some way inhibited from further polymerisation. The first phenomenon sometimes is due to too great an accumulation of substituents, so that the reactivity is so much decreased that the polysulphamides do not react with aldehydes at all. Acetaldehyde forms condensation products with the aniline mono-sulphamides, but not with the corresponding di- and triamides. The same observation was made on some crystallisable products: Benzaldehyde reacts, for instance, with the monosulphamides (giving benzylidene derivatives) but not with polysulphamides. The *ortho*-position

¹ "Bifunctional" groups, as defined by Carothers.

² Details may be found in the papers by G. Walter and collaborators, *Kolloid-chem. Beihefte*, 1933, 37, 343 and 1934, 40, 1.

³ Cf. the dissertation by A. Glück, Univ. of Vienna, 1930. The same rules, based on different experimental materials, were since enounced by other authors as well; cf. further the systematic investigations by Carothers.

of two substituents may also sometimes inhibit reaction. Aniline *o*-sulphamide gives with acetaldehyde only a *mono*-ethylidene compound, whereas the corresponding *meta* and *para*-sulphamides form di-ethylidene derivatives.

In the second case, both groups take part in the formation of the primary condensation product, but despite this fact only soluble and fusible resins are formed as final products. In this case again the *ortho*-position of the substituents accounts for the failure to polymerise. Aniline *o*-sulphamide forms, for instance, only fusible resins, although both groups take part in the primary reaction and produce a dimethylene compound as primary condensation product. The corresponding *meta* and *para* compounds give *methylene-methylol* derivatives as primary condensation products, which are able to polymerise further, until the products become insoluble and infusible.

It is thus proved that *steric hindrance* is responsible for the deviations from the rule.

Table I. shows some of the substances investigated, together with the end-products of their condensation. We investigated the condensation of aryl sulphamides, of the aryl sulphamide-carboxamides, and finally of the aniline sulphamides, with different aldehydes. Where the condensation products are pure methylene compounds, the formulae in the Table give the true elements of the structure forming the polymer. In the cases of more complicated polymers (which are generally methylol methylene compounds) the formulæ give only an approximate idea of the average composition of the resins. So far, neither the exact position of the single substituents, nor the molecular size of these "hardening" resins has been definitely established.

The structure of resins which are formed by the mono-sulphamides was established with a fair degree of certainty (p. 406).

The increase in the number of groups has a double effect. *Firstly*, it increases the number of different possible reactions, and thus leads to a greater variety of polymerisation products—a result favourable to the formation of resins. *Secondly*, it favours the possibility of chain formation, thus favouring the formation of insoluble and infusible products. If one active group alone is present, only one-dimensional chains or simple rings can be formed. The presence of two or more active groups involves the possibility of the formation of networks, complicated ring-systems, or even three-dimensional structures. Staudinger's one-dimensional polystyrenes⁴ remain soluble and fusible even at a very high stage of polymerisation; the urea formaldehyde resins, being the condensation products of a basic molecule with two active groups, are insoluble and infusible, even at a very low stage of polymerisation. This is the result of the ring-structure of these polymers. The capacity to "harden" is therefore due less to a high degree of polymerisation than to the formation of ring-systems,—more to the *constitution* and less to the *molecular size*. Incidentally, the insolubility of "hardening" polymers is, in itself, one of the causes which prevents them from growing further.

⁴ The above discussed rule enabled us to expect divinyl-benzene to yield "hardening" resins. This prediction was confirmed by Staudinger's experiments.

TABLE I.

Amide	Aldehyde.	Composition of the End-product (see p. 404).	Nature of the End-product.		
			Crystallisable.	Resin.	
				Soluble and Meltable.	Insoluble and Unmeltable.
<i>o</i> -toluene-sulphamide	formaldehyde	See p. 406.	Transformation products and components of the resin	+	
<i>p</i> -toluene-sulphamide	"	"		+	
<i>m</i> -benzene disulphamide	"	$C_6H_4(SO_2 \cdot N \cdot CH_3)_2$			+
<i>p</i> -sulphamido benzamide	"	$C_6H_4 \begin{cases} SO_2 \cdot N \cdot CH_3 \\ CO \cdot NH \cdot CH_2OH \end{cases}$ $SO_2 \cdot NH \cdot CH_3 \cdot NH \cdot SO_2$			++*
<i>m</i> -sulphamido benzamide	"	$C_6H_4 \begin{cases} CO \cdot NH \cdot CH_2OH \\ HO_2HC \cdot HN \cdot OC \end{cases} \begin{matrix} C_6H_4 \\ C_6H_4 \end{matrix}$			++
1, 3, 5 benzene trisulphamide	"	$C_6H_3 : (SO_2 \cdot N \cdot CH_3)_2 (NH \cdot CH_2OH)$ $+ C_6H_3 : (SO_2 \cdot N \cdot CH_3)(NH \cdot CH_2OH)_2$			++
same; too short condensation	"	$C_6H_3 : (SO_2 \cdot N \cdot CH_3)(NH \cdot CH_2OH)$ $+ C_6H_3 : (SO_2 \cdot N \cdot CH_3)_2 (N \cdot CH_3)$		+	
Naphthalene-1-monosulphamide	"	$C_{10}H_7 \cdot SO_2 \cdot NH \cdot CH_2OH$ $+ C_{10}H_7 \cdot SO_2 \cdot N \cdot CH_3$		+	
naphthalene-1, 5-disulphamide	"	$C_{10}H_6 \begin{cases} SO_2 \cdot N \cdot CH_3 \\ SO_2 \cdot N \cdot CH_3 \end{cases} \begin{matrix} CH_2 \\ CH_2 \end{matrix} \begin{matrix} O \\ O \end{matrix}$			+
naphthalene-1, 3, 5-trisulphamide	"	$C_{10}H_3 : (SO_2 \cdot N \cdot CH_3)_3 (NH \cdot CH_2OH)$			++
naphthalene-1-monosulphamide at low temp.)	"	$C_{10}H_7 \cdot SO_2 \cdot N \cdot (CH_2OH)_2$	+		
aniline- <i>o</i> -sulphamide	"	$C_6H_5 \begin{cases} SO_2 \cdot N \cdot CH_3 \\ N \cdot CH_3 \end{cases}$		+	
aniline- <i>m</i> -sulphamide	"	$C_6H_5 \begin{cases} SO_2 \cdot N \cdot CH_3 \\ NH \cdot CH_2OH \end{cases}$			+
aniline- <i>p</i> -sulphamide	"	$C_6H_5 \begin{cases} SO_2 \cdot N \cdot CH_3 \\ NH \cdot CH_2OH \end{cases}$			+
aniline-tri-sulphamide (low temp.)	"	$C_6H_5 \begin{cases} (SO_2 \cdot N \cdot CH_3)_3 \\ SO_2 \cdot NH_2 \end{cases}$	+		
aniline- <i>o</i> -sulphamide	acetaldehyde	$C_6H_5 \begin{cases} N \cdot CH \cdot CH_3 \\ SO_2 \cdot NH_2 \end{cases}$	+		
aniline- <i>m</i> -sulphamide	"	$C_6H_5 \begin{cases} N \cdot CH \cdot CH_3 \\ SO_2 \cdot N \cdot CH \cdot CH_3 \end{cases}$			+
aniline- <i>p</i> -sulphamide	"	$C_6H_5 \begin{cases} N \cdot CH \cdot CH_3 \\ SO_2 \cdot N \cdot CH \cdot CH_3 \end{cases}$			+

* Cases of an especially quick and easy "hardening" are marked by two crosses.

Constitution of the Aryl Sulphamide Formaldehyde-resins.

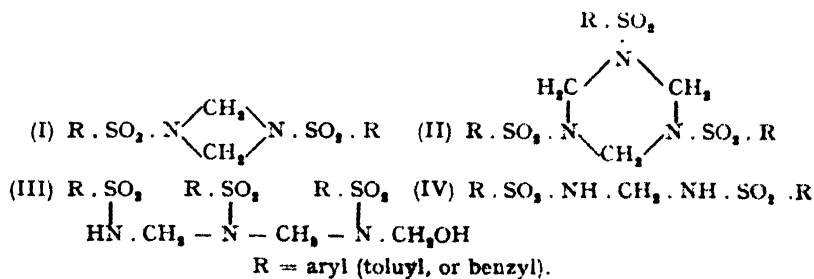
The results will be discussed here only briefly. The aryl monosulphamide formaldehyde resins are transformed by the action of alcoholic hydrochloric acid, as well as by simple heating, into a mixture of crystallisable dimethylene and trimethylene compound (I.) and (II.). These compounds are insoluble in potassium hydroxide, which

TABLE II.

Substance.	Molecular Weight Measured in Phenol (Mean).	Molecular Weight Calculated.
Resin from <i>o</i> -toluene- monosulphamide .	400	—
Component compound (III.)	545	567
Transformation pro- duct (I.)	370	366
Transformation pro- duct (II.)	530	549

easily dissolves the resin itself. They must therefore possess a ring structure. The main component of the resin itself is probably the methylene methylol compound (III.), which yields (I.) by decomposition (together with free sulphamide and formaldehyde), and (II.) by simple dehydration. The compound (III.) was obtained in a crystallisable

form by treating the resin with formic acid. Further, a methylene disulphamide (IV.) was obtained from the resin by extraction with benzene. The structure of all these compounds was established by analysis and determination of molecular weight (see Table II.); their percentage in the resin was determined as well.



The "hardened" (insoluble and infusible) resin obtained from *m*-benzene disulphamide contains polymers of the dimethylene *m*-benzene disulphamide (*cf.* Table I.). Crystallisable products were isolated from a number of hardened resins; we found them to contain CH_2 -groups linked in many different ways. (The naphthalene disulphamide formaldehyde resins contain, *e.g.*, a $\text{CH}_2 \cdot \text{O} \cdot \text{CH}_2$ group (*cf.* Table I.).)

Summary.

As a result of investigations of the condensation products of the aryl mono- and poly-sulphamides, of the amides of the aryl sulphamido-carboxamides and of the aniline sulphamides, it was observed that the presence of more than one active group (*i.e.*, in the case in question, of more than one primary amido-group) is necessary for the formation of insoluble and infusible resins.

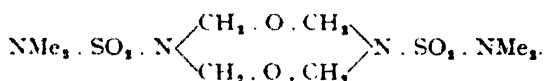
Exceptions occur from steric hindrance (by too copious substitution), and in the cases of *ortho*-substitution which inhibit the primary reaction of the amide with the aldehyde, or diminish the polymerising capacity of the primary condensation product. In Table I., the results of a large number of substances were investigated and rough formulæ given for the average condensation products.

The aryl-monosulphamide-formaldehyde resins were found to contain (or to yield) certain crystallised dimolecular and trimolecular methylene compounds. A number of aryl disulphamide formaldehyde resins were found to contain polymeric dimethylene compounds. Some others are more complicated mixtures, containing methylene and methylol methylene compounds.

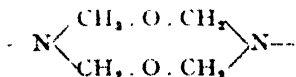
The properties of insolubility and infusibility were found to be due chiefly to an appropriate *constitution* (formation of complicated ring-systems, made possible by the presence of two or more "bi-functional" groups in the basic substance), and much less to a high degree of polymerisation.

GENERAL DISCUSSION.

Dr. F. C. Wood (*Manchester*) said: It is interesting to find the author has suggested the ether linkage $-\text{CH}_2 \cdot \text{O} \cdot \text{CH}_2$ to his Methylene Urea B which Mr. A. E. Battye and I found to occur in the condensation product of unsymmetrical dimethyl sulphamide and formaldehyde giving

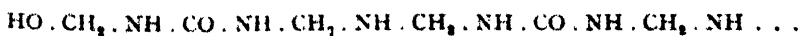


The difficulty in investigating the highly insoluble urea formaldehyde resin compounds seems to indicate that a study of the sulphuryl diamide formaldehyde resin would give further clues to the structure of this type of condensation. I emphasise that the clue to the linkage of the type



came very easily from a brief study of a condensation of dimethyl sulphamide and formaldehyde, which was confirmed by Walter's work later with the sulphonamides, and therefore it is perhaps reasonable to suppose that the more soluble sulphuryl diamide formaldehyde resin would be more amenable to investigations on molecular structure and complexity.

Professor K. H. Meyer (*Genève*) said: I think one ought to consider the reactions between urea and formaldehyde from a more general standpoint, without introducing specific formulæ. If urea reacts with a limited quantity of aldehyde, one can obtain the so-called methylene urea described by Dixon.⁶ This product, described by Walter as amorphous, shows, as Hemmi and Pankow found in Geneva, crystalline interferences. In its solubility it resembles the higher polypeptides of glycine. That is why we assume that it is a somewhat high molecular polymer of the simple and regular formula

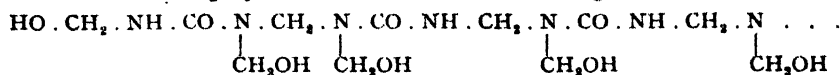


In the presence of an excess of formaldehyde, one obtains water-soluble, highly viscous polymers, described by John.⁶ We admit that the solubility

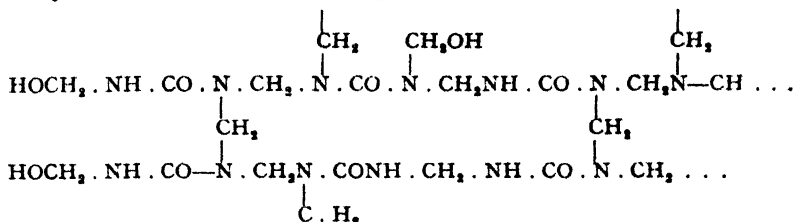
⁶ *J. Chem. Soc.*, 1918, 113, 238.

⁶ *Oestr. Patent*, Nr. 78251, 1918.

in water is provoked by aldehyde groups attached in such a way to the chains as to form polyvalent alcohols of the following kind :



Finally, networks can be formed by cross linkings between the chains :



This product will show the properties of an amorphous insoluble resin. The reactions and the final products are determined by the relative and absolute concentrations, by the temperature, the p_H , etc., and can be modified by adequate adaptation of the conditions.

Dr. G. Walter (*Wien*), in reply to Dr. Wood, said : The conformity he points out was of great interest also to me. It seems that the kind of connection of molecules of which he speaks is not so very rare in condensation products of amides and formaldehyde.

In reply to Prof. K. H. Meyer : It is of great interest to me that Hemmi and Pankow at Geneva have been able to establish crystalline interferences in methylene urea, although other X-Ray workers[†] indicate an opposite result. If, however, Prof. Meyer wishes to apply a somewhat more general point of view (*i.e.* to draw conclusions from the approximate conformity of some of the properties of two polymeric substances that analogic conformity will exist with other important properties, *e.g.* the molecular weight) my very detailed experiments suggest that the greatest precaution must be used in making such comparisons and generalisations. The methylene ureas, however, although in some respects resembling the higher polypeptides of glycine, cannot be assumed to be, necessarily, high molecular polymers : For each of the U.F. condensation products I have examined, the remarkably *low* degree of polymerisation should be emphasised, together with the fact that, despite this, a noticeable formation of ionic complexes or micelles takes place ; this has been determined by me numerically for each and every case and is important for several properties of those products, *e.g.* their small solubility, their infusibility, etc. The probability of the formation of micelles (demonstrated in formic acid solution), the usual weakly acid solutions containing formaldehyde (having a similar D.K. to that of formic acid), and the part played by H-ions in addition to their influence on polymerisation, seem to be connected with the formation of micelles in acid solutions. I am glad to see, however, that Prof. Meyer agrees with my final formula.[‡]

Dr. J. R. Katz, in reply to Dr. Houwink, Dr. Carothers and Dr. Finlayson said : Dr. Houwink brings forward the interesting problem as to what it is we mean by "rubber-like extensibility." Evidently his definition and mine cover different phenomena. From a certain point of view, what we understand by a certain name, is arbitrary ; but, on the other hand, the name ought to cover phenomena so closely related that it is natural to bring just those phenomena, and only those, under that name. Now, rubber-like extensibility being a phenomenon, as yet not yet really understood, it is still to a certain degree arbitrary, what comes under this name, and what not.

[†] See Bois du Chesne, *Kolloidchem. Beih.*, 1932, 35.

[‡] Cf. *This vol.*, p. 390.

In its typical form—as in natural rubber, slightly vulcanised gutta-percha, hydrocarbon polychloroprene, thiokol—we find substances which have an elastic and (approximately) reversible extensibility, permitting an elongation of 300, 500, or even more than 700 per cent. Moreover, these substances are all characterised by the typical form of their stress-strain curves; by the development of heat (Joule-heat) on stretching; by “crystallisation” and by formation of fibre structure, when stretched. In this form I have described the typical phenomenon in my book, published in German in 1934.

Now I do not see that Dr. Houwink has sufficiently proved that any of his three substances: asphalt, glass and the B-state of phenol-formaldehyde resins is a rubber-like substance in the sense of my definition. On the other hand, I recognise with sincere appreciation the value of Dr. Houwink's researches on the large elastic extensibility of his resins in the B-state. I hope he will investigate how far those other properties are present which I consider as characteristic for real rubber-like extensibility. Let us not forget that there are a number of “rubber-like” substances which do not show some of the characteristic qualities, or show them only in a weakened degree. For instance, isoprene-heat-polymerisate has not shown “crystallisation” on stretching; yet it develops a certain amount of heat and a certain amount of fibre structure when stretched. It would be very interesting, if Dr. Houwink would compare such substances with the B-resins mentioned above, and see if perhaps these uncharacteristic poor “rubber-like” substances stand half-way between real rubber and B-resins.

Dr. Carothers' doubt, whether the crystallinity of high polymeric substances is a real crystallinity raises a problem which seemed very difficult to answer when, first, X-ray spectrography was applied to substances of this kind, and which, in the case of rubber, is even now not entirely clear to me. I myself questioned whether the “crystallisation” of rubber, when stretched, is a real crystallisation; I gave expression to this doubt when writing my first publication about the phenomenon⁴² and even questioned whether we may not have to do with a new type of substances, which I called pseudo-crystalline-amorphous ones. The structure of a liquid under 20,000 atmospheres pressure (when it retains a certain amount of plasticity under this high pressure) is the closest comparison. The molecules can be forced into a three-dimensional arrangement, without being *entirely* comparable with a real crystal. In the case of rubber the form of the molecule—a long thread—may be particularly favourable for the development of such a state; as the threads are straightened by extension, they are pressed laterally against one another, so that the fundamental units of the molecules are forced into the closest possible packing.

On the other hand, we must admit that, after twelve years during which X-ray spectrographical research, all the facts have proved more and more explicable by the hypothesis that where there is a crystalline X-ray pattern, we have to do with real crystals; with a new phase in the sense of the phase rule. In the case of rubber, however, I admit that the clear *discontinuity* in the anisotropy curve (see Fig. 6) at the critical elongation suggests clearly—together with the X-ray data—that we have to do with a real change from an amorphous into a crystalline phase. Studying the influence of temperature on this critical elongation, Professor Ornstein (Utrecht) has even been able to apply the Clapeyron equation to it. In the case of crystalline phases which can only exist under very high pressures (several of the “ices,” for instance) their equilibrium conditions are governed by the phase rule; which seems to indicate clearly that they are real crystalline phases.

⁴² *Naturwissenschaften* 1925, 13, 411.

I soon hope to publish about rubber-like vulcanised gutta-percha hydrocarbon and its analogy with natural rubber.

I now come to the very important question raised both by Professor Kurt H. Meyer and Professor H. Mark: *what degree of certainty can be attached to their calculations of the crystalline lattice of high polymeric substances and of the position of the molecules therein.* These calculations in 1928 gave a great impetus to our understanding of the high polymeric substances and at that time provided one of the strong arguments for the long chain molecule. All agree that their work had the merit of putting us on the right track. But we are now in 1935, and I think it is surprising that no one has *investigated, as impartially as possible, to what extent their arguments of 1928 were convincing, and to what extent there is ground for doubt.*

Professor Mark admits uncertainty, but he says that we may attribute to these models "a somewhat high degree of truth." And he agrees with me that we must improve these ideas here and there, and that more or less important changes may have to be made; although he states, too, that in his opinion the present point of view will not have been entirely changed when the full solution is found. On this point I agree a good deal with him.

Professor Meyer believes that when he uses thin films in which there is not only a parallel orientation of the crystals in one direction, but also an orientation in the plane perpendicular to this axis, one can calculate with *certainty* the three periods of identity and the elementary cell. The same thesis was defended by an author who reviewed my book in *Z. Elektrochemie*, 1935. In my opinion, both authors are wrong in making this statement. They might have been right, if the X-ray interferences of the high molecular weight substances were very sharp (like those of NaCl, CaCO₃, etc.). But with the lack of sharpness of the interferences, as observed in cellulose, silk fibroin and all such substances, we never can exclude the possibility that what we consider as one interference may be made up from more than one. Moreover the orientation is often not so perfect as we would desire. These uncertainties affect the calculation of the elementary cell. Moreover all interferences with an angle of deviation θ larger than 30°-40° are completely absent, which excludes the possibility of control by higher orders of reflection; I regret the other authors mentioned do not agree with my reservation, which seems so plain to me.

Both Professor Meyer and Professor Mark emphasise that the certainty of their special models arises not only from the X-ray data, but also because the conclusions drawn from them are strengthened by chemical evidence. I am unable, however, to rate the degree of certainty they have reached as highly as they do.

I wish chiefly to emphasise the need of work which does not try merely to confirm or to attack their point of view, but which seeks an impartial discussion of the following points:—

(a) Description and measurement of all the interferences observed; how far are we certain that *all* the interferences have been found; that they are not conglomerates of more than one interference; that they are not due to continuous radiation; what "doubled interferences" mean, etc.

(b) Checking of this information by oblique exposures; and by exposures in different directions of films showing orientation in more than one direction; careful discussion on the relative uncertainty of all the factors involved.

(c) Calculation of the elementary cells; *how many* and *which different* solutions accord with all the facts mentioned under (a) and (b); *which* solution is preferable and *why*; which conclusions can be drawn from chemical or analogous evidence, and their relative cogency compared with evidence drawn from only X-ray data.

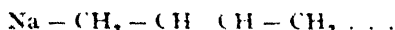
(d) Accurate measurement of the relative intensities (in pure monochromatic light) of all the interferences observed. The old rule that the relative position of atoms in the elementary cell requires necessarily such intensity measurements should not be given up in the more difficult case of high polymeric substances.

(e) The position of the molecules within the elementary cell. Chemical and analogous evidence will be needed for a good estimate. Other possible solutions should, however, be discussed, and compared with the intensity measurements, with the chemical evidence, etc.; and the relative probability of the different solutions should be made clear.

Meantime we should seek to prevent the presentation, in elementary text-books and in biological, biochemical or technical literature, of merely probable solutions, as though they were as good as proven. In every scientific subject there are three typical phases of development. In the first one collects interesting facts and seeks to co-ordinate them; in the second one possible explanation of the whole mass of facts is presented; in the third we have several such explanations, and by an *experimentum crucis* can make a choice between them, which is to be considered as a certainty. The whole subject I have discussed above is really only somewhat fully developed into the second stage; whilst it is more and more quoted as being in the third stage. It is against this exaggeration of certainty that I have felt it my duty to warn you.

If preliminary, and still uncertain solutions of the problem are so presented they may be very useful for the growth of the subject. But they should be so presented or quoted and with that degree of uncertainty.

Professor Medvedev, in reply (see page 296) (*communicated*) the opinion of Bergmann,* that the polymerisation of 1, 3-butadiene† takes place by way of a mono-sodium compound, can hardly be concordant with the observed results without a special strained interpretation. The supposed mono-sodium compounds of Bergmann of the type:



are evidently not stable, and cannot exist for long as free radicals.

In the case of an artificial stoppage of the reaction (*e.g.*, evacuation of the butadiene during polymerisation in the gaseous phase) these radicals would dimerise or be subjected to some other transformation, and the renewal of the process would not be possible. However, our experiments show that interruption, even for many hours, of the polymerisation process does not show a marked change in the kinetics of the process. Formation of the mono-sodium compound was used by Schlenk to explain the appearance of dimerisation by the action of the alkali metals on non-symmetrical substituted ethylene. On the other hand, Ziegler‡ showed that, by the action of sodium or lithium on 2, 3-di-methyl butadiene and the decomposition of the formed products by water, tetra-methyl ethylene is formed; this is a very substantial argument in favour of the formation of di-sodium compounds.

It is extremely possible that the major part of the polymerisation process takes its course by means of a chain mechanism in the same sense as was formulated in the discussion by Rideal and Mark. Polymerisation of di-ene hydrocarbons in the presence of the alkali metals, however, is a particular case, which differs in the fact that the growth of the polymerising molecule takes place as the result of a series of reactions in which the union of the monomer to the stable sodium-organic compound occurs. This monomer is probably activated in the process of "solution" in the polymer.

One of the results of the stability of the intermediate products ("active centres") is the circumstance that the reaction "chain" does not break and the polymerisation process, after the attainment of a stationary stage, proceeds with a constant rate for an indefinitely long time in spite of the fact of interruptions.

Dr. H. B. Welser (Houston, Texas), in reply (see page 377) said: It is interesting to note that Pauli never considered the formula



* Bergmann builds his scheme on the example of di-methyl butadiene, but we studied the polymerisation of 1, 3-butadiene.

† *Lieb. Annalen* 511, p. 64, 1934.

for a ferric oxide sol as essentially correct. The trouble is that this and similar formulas for other oxide sols have been repeated and copied so many times in both text-books and papers by Pauli and others, that most people think that Pauli believes them to be essentially correct. Indeed, last year at the General Discussion on Colloidal Electrolytes before the Faraday Society, the neutral part and the charged ionic group of a ferric oxide sol are given by Pauli as $\text{Fe}(\text{OH})_3$ and FeOCl , respectively. Since $\text{Fe}(\text{OH})_3$ has not been prepared and FeOCl is formed only under special conditions at high temperatures, we may be reasonably sure that neither is present in the sol as ordinarily prepared. It is not obvious what is gained by assuming the presence of an ionogenic complex such as FeOCl on the surface of the sol particles when ferric chloride and hydrochloric acid, which are known to be present, will serve equally well as stabilising electrolytes for the sol. Just because the p_H value of an oxide sol is 6, it does not follow, as Dr. Eirich believes, that hydrochloric acid cannot be the stabilising electrolyte in such a sol. As a matter of fact, the p_H value of the sol would be 7 if all the stabilising hydrogen ions were adsorbed on the surface of the particles. It is probable that the stabilising electrolyte in Pauli and Schmidt's sol formed in the presence of dilute aluminum chloride is largely the latter salt rather than hydrochloric acid. There is no apparent justification for assuming that the stabilising electrolyte is a basic salt such as AlOCl whose existence in the sol or elsewhere has not been established. Since the neutral part of the oxide sols formed in the presence of chloride contain more or less of the latter element, the constitution is represented by some point in the three-component diagram



This does not mean that the sol contains free hydrochloric acid.

In Pennycuik's platinum sols to which Dr. Eirich refers, the contra ion is hydrogen ion, just as in ferric oxide and alumina sols the contra ion is usually chloride ion. When neutral salts are added to platinum sols an exchange adsorption takes place between the cation of the added salt and the hydrogen ion. This causes the p_H value of the sol to decrease rather than to increase. The acidic oxide on the surface of the particles causes hydrolytic cleavage of some salts, the base combining with the acidic oxide. This process likewise tends to decrease rather than to increase the p_H value of the sol.

ERRATA

- Page 53. The last two paragraphs should be transposed.
- Page 252. In third complete paragraph: *For* "specific refractive molecular weight" *read* "specific refraction—molecular weight."
- Page 257. In second paragraph, line 2, insert semicolon after "materials."
- Page 290. In second and third complete paragraphs: *For* "kinetic" *read* "kinetics of the."
- Page 303. Below Fig. 3: *For* "gm. per litre" *read* "gm. per 100 c.c."
- Page 305. In 3rd and 4th lines from bottom of first paragraph: *For* " $(n_0 - n_a)'$ " *read* " $(n_\gamma - n_a)'$ "

A METHOD OF ANALYSIS OF HEAVY WATER.

BY ADALBERT FARKAS.

Communicated by ERIC K. RIDEAL.

Received 13th November, 1935.

Whilst several methods¹ are available for the analysis of heavy water, the micro-thermo-conductivity method^{2, 3} is so convenient for the analysis of hydrogen-deuterium mixtures that it seemed desirable to attempt an application of this technique to heavy and ordinary water without involving the decomposition on a hot tungsten wire.³ The method is based upon the following principles.

If water containing W_D per cent. D be brought into equilibrium with its own vapour and with hydrogen, these will contain respectively V_D per cent. and G_D per cent. deuterium.⁴ We denote by f the ratio of the vapour pressures of H_2O and D_2O and K_3 the equilibrium constant of the reaction

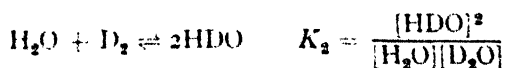
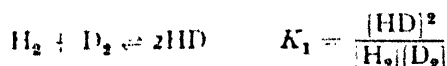


$$\text{i.e.,} \quad K_3 = \frac{[HDO][H_2]}{[H_2O][HD]}.$$

Then

$$V_D = \frac{W_D}{100 - W_D f + W_D} \quad \frac{G_D}{100 - G_D} = K_3 \frac{W_D}{100 - W_D},$$

if we assume⁴ that the equilibrium constants of the reactions



are $K_1 = K_2 = 4$.

If the liquid water be maintained at 20° C. and equilibrium in the gas phase be established on a hot platinum wire at 1000° K. we obtain the following D-contents for the hydrogen in equilibrium with water of different D-contents.

According to Lewis and Macdonald⁵ $f = 1.15$ at 293° K. K_3 has

¹ A. Farkas, *Parahydrogen, Orthohydrogen and Heavy Hydrogen*, the Cambridge University Press, 1935.

² A. Farkas *Z. physik. Chem.*, 1933, **22B**, 344.

³ A. Farkas and L. Farkas, *Proc. Roy. Soc.*, 1934, **144A**, 467.

⁴ A. Farkas and L. Farkas, *Trans. Faraday Soc.*, 1934, **30**, 1071.

⁵ G. N. Lewis and R. T. Macdonald, *J. Amer. Chem. Soc.*, 1934, **55**, 3057.

not yet been determined accurately at 1000°K .; extrapolation from the equilibrium measurements ^{4,6} gives us the value 1.1.

TABLE I.

D-content of the Water (W_D), in Per Cent.	D-content of the Vapour (V_D), in Per Cent.	D-content of the Gas (G_D), in Per Cent.
0	0.0	0.0
25	22.5	20.9
50	46.5	44.1
75	72.4	70.5
100	100.0	100.0

Thus we can easily calculate from the D-content of the gas in equilibrium (under the given conditions) with the water to be analysed the unknown D-content of the latter.

The experimental arrangement is shown in Fig. 1.

The cell is 10 cms. long and 5 mm. in diameter. After having placed about

0.1-0.2 c.cm. of water in tube A, the cell is exhausted and hydrogen (or deuterium) introduced at about 10 mm. Hg and then the spiral is heated. By means of the capillary lock L from time to time small samples of gas are extracted and their D-content analysed by the micro-thermo-conductivity method. Table II, shows the results obtained with different samples of heavy water of known D-content (determined by density measurements).

It will be noted that the final value is reached within a few minutes and is independent of whether we start with pure hydrogen (experiment 3) or with deuterium (experiment 4). The experimental figures for the equilibrium D-content are in satisfactory agreement with the calculated values (column 5), the average error being 1.5 per cent. The accuracy of the measurement might be affected by the following sources of error: the cell is not absolutely dry (from previous experiment), the water contains gases (including such as, *e.g.*, HCl) or evaporable organic compounds which can be decomposed by the hot filament, there is too little water available for the analysis (see below). On the other hand substances (whether present dissolved or undissolved) which have no appreciable vapour pressure, or the hydrogen dissolved in the platinum wire, do not influence the accuracy of the analysis.

The minimum quantity of water required for a determination is limited by the total amount of hydrogen admitted. The D-content of the water will not change appreciably if the equivalents of water and hydrogen present are in the ratio 500:1 (1 mg. water being equivalent approximately to 1 c.c. of H_2 , N.T.P.). In this particular cell 0.2 c.c. of H_2 , N.T.P. (or D_2) were introduced and at least 0.1 g. of water was used for each measurement. It is, however, a simple matter to reduce this quantity to 0.01 g. by using 1.5 c.c. cell (*e.g.*, 4 mm. diameter and 5 cms. long). The accuracy of the analysis can be increased by empirical calibration.

The present method of analysis is specially suitable for investigating the interchange of hydrogen and deuterium atoms between water and other substances (provided the latter have no appreciable vapour pressure) without the need of separating the water for each determination. It possesses advantages if only small amounts of water are available (*e.g.*,

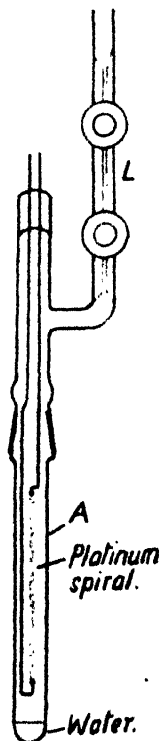


FIG. 1.

⁴ R. H. Crist and G. A. Dalin, *J. Chem. Physics*, 1934, 2, 735.

TABLE II.

No.	D-content of the Water (W_D), in Per Cent.	Time in Mins.	D-content of the Gas (G_D), in Per Cent. Observed.	D-content of the Gas (G_D), in Per Cent. Calculated.
1	29.5	0	0.0	25.3
		3	21.5	
		8	25.2	
		21	25.1	
2	50.2	0	0.0	44.4
		2	43.0	
		6	45.5	
		15	44.5	
3	76.4	0	0.0	71.9
		1	62.0	
		3.5	73.2	
		8	72.8	
4	70.4	0	95.0	71.9
		1	79.2	
		5	72.7	
		11	73.0	
5	97.7 *	0	0.0	97.1
		3	94.5	
		9	95.5	

in biochemical problems) or if a series of analyses have to be made when other methods would take too much time.

The following experiment may be cited as an example for the application of the present method. 1.032 g. NH_4NO_3 were dissolved at 20°C . in 0.5 c.c. of 29.5 per cent. heavy water. The D-content of the solution was found to be 15.5 per cent.

Since 1.032 g. of NH_4NO_3 are equivalent to 0.465 g. or 0.466 c.c. water the D-content of the ammonium nitrate (S_D) was

$$\frac{(29.5 - 15.5)0.50}{0.466} = 15.0 \text{ per cent.},$$

i.e., practically the same as that of the water. Consequently the quantity $\frac{W_D(100 - S_D)}{S_D(100 - W_D)}$ is practically = 1.

This result is in agreement with the earlier experiments of Bonhoeffer and Brown,⁷ who obtained a value for the system $\text{NH}_4\text{Cl}/\text{H}_2\text{O}$ of 1.25 which they regarded as too high.

Summary.

Description of a method for the analysis of heavy water based on an exchange reaction with hydrogen.

The author is very much indebted to Professor E. K. Rideal, F.R.S., for his interest in these experiments and to the Imperial Chemical Industries Ltd. for financial assistance.

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Cambridge.*

* This determination was made a few months ago. The actual D-content was probably slightly less owing to manipulations with the water.

⁷ *Z. Chemie*, 1933, 23B, 171.

THE CATALYTIC INTERACTION OF AMMONIA WITH DEUTERIUM.

BY ADALBERT FARKAS.

Communicated by ERIC K. RIDEAL

Received 13th November, 1935.

In a previous communication ¹ an account was given of an exchange reaction between deuterium and ethylene. A number of similar reactions involving organic substances have since been investigated.² The subject matter of this paper deals with an exchange reaction between ammonia and deuterium which may be written



and which occurs at the surface of an iron catalyst.³ Apart from it being representative of a new group of exchange reactions it is of interest in connection with the catalytic synthesis of ammonia.

Experimental.

In previous experiments ⁴ it was found that even apparently outgassed material contains a certain amount of hydrogen absorbed in such a form as to become apparent by an exchange reaction when brought into contact with deuterium. A catalyst possessing a negligible amount of such occluded gas can be prepared by forming a metallic mirror by evaporation

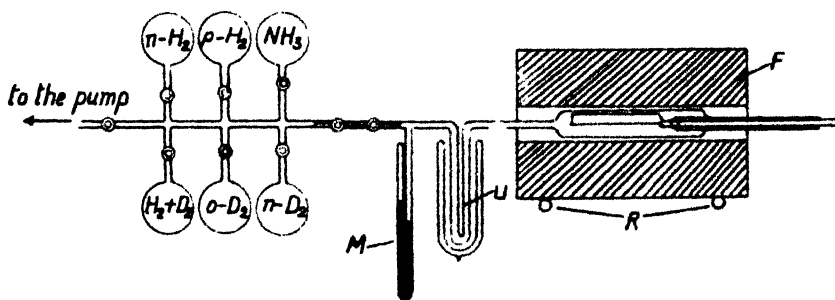


FIG. 1.

of an iron wire. Such mirrors when deposited at room temperature are readily prepared, reproducible in activity, reasonably active and stable.

The experimental arrangement is shown in Fig. 1. The reaction vessel (12 cms. long and 2 cms. in diameter) contained an axially mounted iron (electrolytic) wire 10 cms. long and 0.2 mm. in diameter arranged with leads in the usual way so as to permit of electric heating. The U-tube U

¹ A. Farkas, L. Farkas and E. K. Rideal, *Proc. Roy. Soc.*, 1934, 146A, 630.

² I. Horiuti and M. Polanyi, *Trans. Faraday Soc.*, 1934, 30, 663, 1164.

³ Cf. also H. S. Taylor and J. C. Jungers, *J. Amer. Chem. Soc.*, 1935, 57, 660.

⁴ A. Farkas and L. Farkas, *Trans. Faraday Soc.*, 1935, 31, 821.

was cooled to -50°C . in order to keep tap grease and mercury from poisoning the catalyst. With these precautions the catalyst did not markedly decrease even after a week's use at 200°C .

Before deposition of the catalyst the reaction vessel was thoroughly outgassed in the furnace F at 350°C . (or using Pyrex vessels at 500°C .) the wire was being maintained at 900°C . The furnace was then removed by means of the rollers R and the wire heated to 1100° – 1200°C . to evaporate the iron. This temperature was maintained (with continuous exhaustion) until a uniform mirror was formed. If the catalyst has once been poisoned (e.g., by admission of air to the reaction vessel) a new catalyst was prepared by evaporating fresh iron in the same vessel. The evaporation process could be repeated four or five times before the wire broke.

In order to obtain more information about the interaction of hydrogen and ammonia on this catalyst, the *ortho-para*-conversion and interaction of hydrogen and of deuterium and the decomposition of ammonia were investigated in addition to the exchange reaction between ammonia and deuterium.

To investigate the exchange reaction and the *ortho-para*-conversion, the micro-thermoconductivity method was employed, ammonia being frozen out in a trap cooled by liquid air.⁵ The decomposition of ammonia was determined by extracting samples of gas from the reaction vessel and measuring the pressure caused by this sample after freezing out the ammonia.

The following gases were used: ammonia (purified by fractional distillation *in vacuo*), deuterium (80 to 100 per cent. D), ortho-deuterium⁶ (100 per cent. D, prepared by adsorption on charcoal at 20°K . and subsequent evaporation), parahydrogen (prepared in a similar way) and a mixture of hydrogen and deuterium (containing only H_2 and D_2 molecules). All gases were free from oxygen, the hydrogens were initially purified by passage through palladium. The pressures of the gases admitted into the reaction vessel were measured by the manometer M (see Fig. 1).

The experiments to be described were carried out partly on the same catalyst, partly on different catalysts.

The Exchange Reaction between Ammonia and Deuterium.

Since in all experiments the rate of the exchange reaction was determined by measuring the decrease in the D-content of the deuterium originally added special care had to be taken to avoid the following sources of error. The D-content of the deuterium may decrease by an exchange reaction with hydrogen occluded or absorbed by the catalyst or formed by a catalytic decomposition of ammonia taking place on the surface of the catalyst. Separate experiments excluded the former

TABLE I.

Temperature $^{\circ}\text{C}$.	Previous Treatment of the Catalyst.	Minutes.	Per Cent. D.
230	30 per cent. D	0	96
		5	96
		12	95
230	96 per cent. D	0	0
		0	1
		15	2

possibility since—as has already been mentioned—no interchange could be observed with gases occluded by these catalysts. Thus there was only

⁵ (a) A. Farkas, *Z. physik. Chem.*, 1933, 22B, 344; (b) A. and L. Farkas, *Proc. Roy. Soc.*, 1934, 144A, 467.

⁶ A. Farkas, L. Farkas and P. Harteck, *Proc. Roy. Soc.*, 1934, 144A, 481
A. and L. Farkas, *ibid.*, 1935, 152A, 124.

a negligible decrease in the D-content of deuterium brought into contact with a catalyst previously exposed to hydrogen and practically no formation of deuterium after the catalyst has been in contact with deuterium (see Table I.).

By experiments on the rate of decomposition of ammonia it was found that in no case could the amount of uncondensable products formed account for more than a small fraction of the decrease in the D-content actually observed. On the same catalyst, for example, as referred to in Table II. at 233° C. and 15 mm. Hg of NH₃, the amount of uncondensable gas formed was 3 mm. in thirty minutes, *i.e.*, very little in comparison with the rate of the decrease in the D-content (see Table II.).

TABLE II.

234° C., 10 mm. NH₃ + 15 mm. D₂

Minutes.	D-content in Per Cent.
0	96
0	34
15	23

Fig. 2 shows that the decrease in the D-content is actually due to an exchange. Curve *a* indicates the change in the D-content of 30 mm. deuterium when mixed with 26 mm. NH₃ at 233° C. After thirty minutes the ammonia was frozen out (in trap U, Fig. 1) the deuterium pumped out and 22 mm. of hydrogen added. The flat portion of the curve *b* shows once more that no exchange reaction occurs in the absence of ammonia but sets immediately when the ammonia is evaporated (in the twelfth minute). In this case the D-content of the hydrogen added naturally increases at the expense of the "heavy" ammonia formed in the previous experiment.

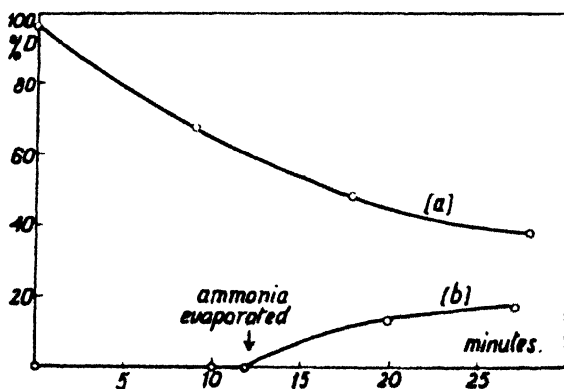
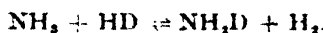


FIG. 2.

The equilibrium constant of the reaction ⁷



$K = \frac{[\text{NH}_2\text{D}][\text{H}_2]}{[\text{NH}_3][\text{HD}]}$ could not be accurately determined by measuring the final D-content of a mixture of ammonia and deuterium for the following reason. The value of the equilibrium constant obtained is very sensitive to the final D-content observed and an inaccuracy of a few per cent. in the determination of the final D-content may cause a considerable error in the determination of the

TABLE III.

EQUAL PRESSURES OF D₂ (100 per cent. D) and NH₃.

Final D-content in Per Cent.	K.	$2K/3 = (\text{H}/\text{D})_{\text{A}} \cdot (\text{D}/\text{H})_{\text{B}}$
40	1.5	1.0
35	2.1	1.5
30	3.0	2.0

equilibrium constant (see Table III.).

⁷ A. Farkas, *J.C.S.* (in the press).

In the third column $(H/D)_h$ and $(H/D)_a$ represent the ratio of the H- and D-content in the hydrogen and ammonia respectively.⁷ The inaccuracy in the determination of the final D-content is due to the slight decomposition of ammonia (especially the formation of nitrogen). Another source of error is the strong adsorption of ammonia on the glass walls especially on those cooled to low temperatures (U tube), and thus the amount of ammonia taking part in the interchange is actually more than that calculated from the pressure readings. Both sources of error tend to produce a final D-content which is too low or an equilibrium constant which is too high. After allowing for this inaccuracy it was found that the equilibrium is definitely larger than the classical value of $3/2$ being at 220° - 230° C. about 2 to 3.* This provisional result which is in agreement with theoretical calculations requires confirmation by more accurate experiments.⁸

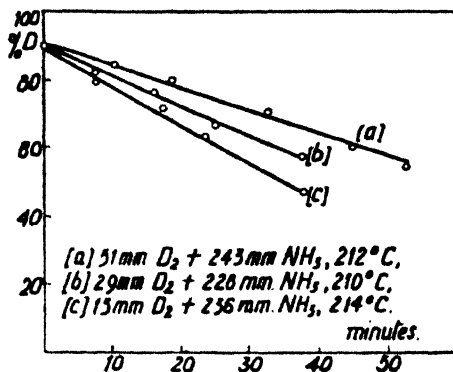


FIG. 3.

In order to exclude any uncertainty in the value of K the dependence of the rate of the exchange on pressure was investigated in mixtures with excess of ammonia in which the equilibrium D-content is very low.

The progress of the interchange at 200° - 210° C. at different deuterium pressures and constant ammonia pressures and at different ammonia pressure and constant deuterium pressures is shown in Figs. 3 and 4. It will be seen that whereas the relative rate of the interchange remains

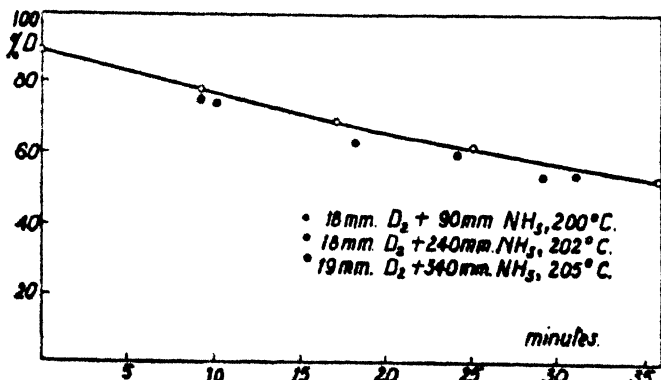


FIG. 4.

unaltered by changing the ammonia pressure, it decreases with increasing deuterium pressure.

In another series of runs the dependence of the rate of interchange was investigated at a varying total pressure

but at approximately the same ratio $NH_3 : D_2$, see Table IV.

The measure for the relative rate of the exchange is the time (τ , in minutes) in which the original D-content has decreased by 25 per cent. and is given in column 5, whereas the measure for the absolute velocity being proportional to the deuterium pressure and $1/\tau$ is listed as P_{D_2}/τ in

* Such a value follows indirectly from exchange experiments between heavy water and ammonium salts. (Bonhoeffer and Brown, *Z. physik. Chem.*, 1933, 23B, 171, and A. Farkas, *Trans. Faraday Soc.*, in the press.)

⁸ Cf. also K. Wirtz, *Naturwiss.*, 1935, 23, 271.

TABLE IV.

Temperature C.	Pressure of Deuterium in mm. Hg (P_{D_2}).	Pressure of Ammonia in mm. Hg (P_{NH_3}).	P_{NH_3}/P_{D_2} .	25 Per Cent. Decrease in the D-content Reached in (τ).	P_{D_2}/τ .
203	17	64	3.8	11 mins.	1.55
201	39	110	3.0	17 ..	2.29
203	54	246	4.5	22 ..	2.45
208	82	326	4.0	29 ..	2.83

column 6. Similar data for the experiments shown in Figs. 3 and 4 are given in Table V.

TABLE V.

Temperature °C.	Pressure of Deuterium in mm. Hg (P_{D_2}).	Pressure of Ammonia in mm. Hg (P_{NH_3}).	25 Per Cent. Decrease Reached in (τ).	P_{D_2}/τ .
200	18	90	20 min.	0.90
202	18	245	19 ..	0.95
205	19	340	17 ..	1.11
214	13	236	17 ..	0.77
210	29	228	23 ..	1.26
212	51	243	31 ..	1.64

From Tables IV. and V. we note that the absolute rate of the exchange reaction, *i.e.*, the number of atoms exchanged is practically independent of the ammonia pressure but increases approximately with the square root of the deuterium pressure.

The dependence of the rate of interchange on temperature is shown in

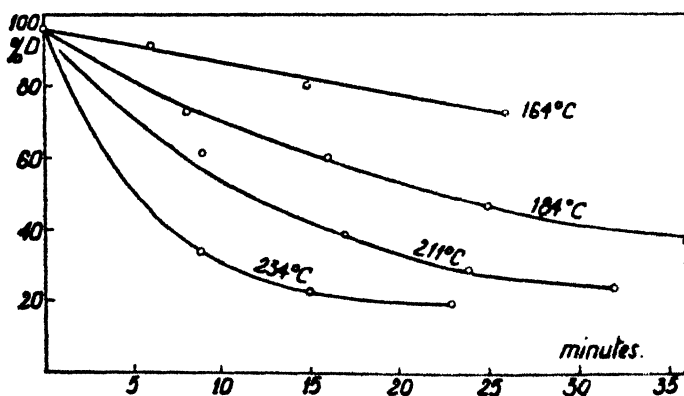


FIG. 5.

Fig. 5 for the temperature region 164°-234° C. and at 15-17 mm. of D_2 and NH_3 . (The curves for 211° and 234° refer to the catalyst in a slightly less active form.)

The apparent energy of activation (E)

was calculated from the dependence of the rate of exchange on temperature with the equation

$$\frac{d \log 1/\tau}{dT} = \frac{E}{RT^2}$$

τ denoting the time (in minutes) in which the original D-content has decreased by 25 per cent. (see Table VI.).

TABLE VI.

Temperature °C.	Pressure of Deuterium in mm. Hg (P_{D_2}).	Pressure of Ammonia in mm. Hg (P_{NH_3}).	τ in Minutes.	Energy of Activation in Kg Cals.
170	15	15	20	14.4
196	15	15	8	
164	15	14	26	18.9
184	15	15	10	
201	14	16	5.5	
211	15	17	6.5	13.1
234	16	15	3.5	
			Mean	15.0

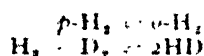
The Ortho-para-conversion.

In a series of previous publications* it was shown that the catalytic ortho-para-hydrogen conversion on metals involves an atomic mechanism.

It was important to obtain some information about the catalytically active adsorption layer by this method since the "sorptive" capacity of this catalyst was hardly measurable. (There is no necessary connection between adsorptive capacity and catalytic activity. High adsorptive capacity is not always indicative of a high catalytic activity.)

On a fresh catalyst the ortho-para-hydrogen conversion occurred at room temperatures and a few mm. Hg pressure at a high velocity equilibrium being established within a few minutes. Under similar condition there was, however, no exchange reaction to be detected even after several hours.

Although it has already been shown that the reactions^{10, 16}



proceed on a catalyst by the same mechanism namely by dissociation into atoms, it seemed desirable to show this including also the reaction $o\text{-D}_2 \rightleftharpoons p\text{-D}_2$ for the catalyst actually employed. Fig. 6 shows the establishment of the equilibrium in these reactions at 10 mm. Hg pressure and 20° C the logarithm of the "distance" from equilibrium (u), (taken as 100 at the beginning and 0 at the end), being plotted against the time.

It will be noticed that though the individual reaction rates are different,

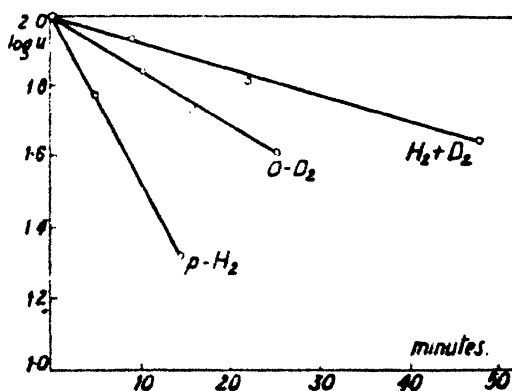


FIG. 6.

* Bonhoeffer and Farkas, *Z. physik. Chem.*, 1931, 12B, 231; A. Farkas, *ibid.*, 1931, 14B, 371; Bonhoeffer, Farkas and Rummel, *ibid.*, 1933, 21B, 225; Bonhoeffer and Farkas, *Trans. Faraday Soc.*, 1932, 28, 242; A. Farkas, *Ortho-hydrogen, Parahydrogen and Heavy Hydrogen*, The Cambridge University Press, 1935.

¹⁰ E. Fajans, *Z. physik. Chem.*, 1935, 28B, 239.

the relative rates being 5 : 2 : 1 for $p\text{-H}_2$, $o\text{-D}_2$ and $\text{H}_2 + \text{D}_2$ respectively, these three redactions proceed with a very similar speed.

The temperature coefficient for these reactions are likewise very similar, indicating that in these processes practically the same energy of activation

TABLE VII.

Reaction.	Temperature C.	Half-Life Time in Minutes.	Energy of Activation in Kg Cala.
$p\text{-H}_2 \rightleftharpoons o\text{-H}_2$ * at 18 mm. Hg.	85	8.5	8.1
	100	5	
	130	3	
	160	1.5	
$o\text{-D}_2 \rightleftharpoons p\text{-D}_2$ at 12 mm. Hg.	20	20	8.4
	40	8	
$\text{H}_2 + \text{D}_2 \rightleftharpoons 2\text{HD}$ at 11 mm. Hg.	20	40	9.0
	40	15	

* Catalyst different.

is involved (see Table VII.). As expected slightly higher values are obtained for the reactions involving deuterium.

We note that this apparent energy of activation is considerably lower than that found for the exchange reaction between deuterium and ammonia. This

difference in the energies of activation is responsible for the fact that the conversion reaction takes place readily at temperatures which are 200°C . below those necessary for the exchange reaction.

It was found that the presence of ammonia inhibited the conversion of *para*-hydrogen, the inhibiting effect being dependent on the pressure of ammonia. Fig. 7 shows this effect at 82° and 122°C . and 15 mm. Hg of *para*-hydrogen, the velocity of the conversion in the absence of ammonia being taken as unity. The inhibiting effect at these temperatures is reversible i.e., the original activity is restored as soon as the ammonia is removed.

In spite of this inhibition the conversion reaction is even in the presence of NH_3 much faster than the exchange as clearly shown by the following experiment.

In the thermo-conductivity cell employed for the analysis of hydrogen and deuterium mixtures hydrogen, normal deuterium and *ortho*-deuterium had the following "resistance" values (i.e., the resistance of the wire in the thermo-conductivity cell when heated in the gas),

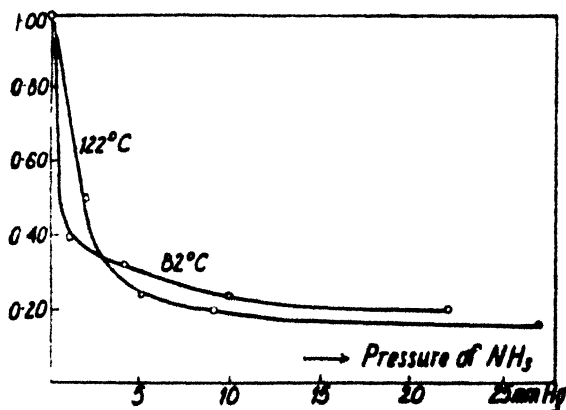


FIG. 7.

	Ω .	$\Delta\Omega$ relative to $n\text{-D}_2$
normal hydrogen ($n\text{-H}_2$)	91.70 ohms.	- 12.19 ohms.
normal deuterium ($n\text{-D}_2$)	103.91 "	0.00 "
<i>ortho</i> -deuterium ($o\text{-D}_2$)	106.39 "	+ 2.48 "

Thus it was easy to show how much more quickly the conversion of *ortho*-deuterium proceeded than the interchange reaction in a mixture of $o\text{-D}_2 + \text{NH}_3$.

Fig. 8 shows the progress of these reactions in a mixture of 12 mm. $o\text{-D}_2 + 15$ mm. NH_3 over the temperature range 20° to 155°C ., the differences in the resistance values (relative to $n\text{-D}_2$, $\Delta\Omega$) being plotted as a function of time. At 155°C . there is slight exchange reaction to be observed proceeding a hundred times more slowly than the conversion; at 82°C ., however, there is practically no exchange reaction.

Whereas the inhibition of the $p\text{-H}_2$ conversion is reversible at 80°C . and upwards, at room temperatures the poisoning effect of ammonia persists even after removal of that gas. When ammonia is admitted to a fresh catalyst there is an immediate formation of some uncondensable

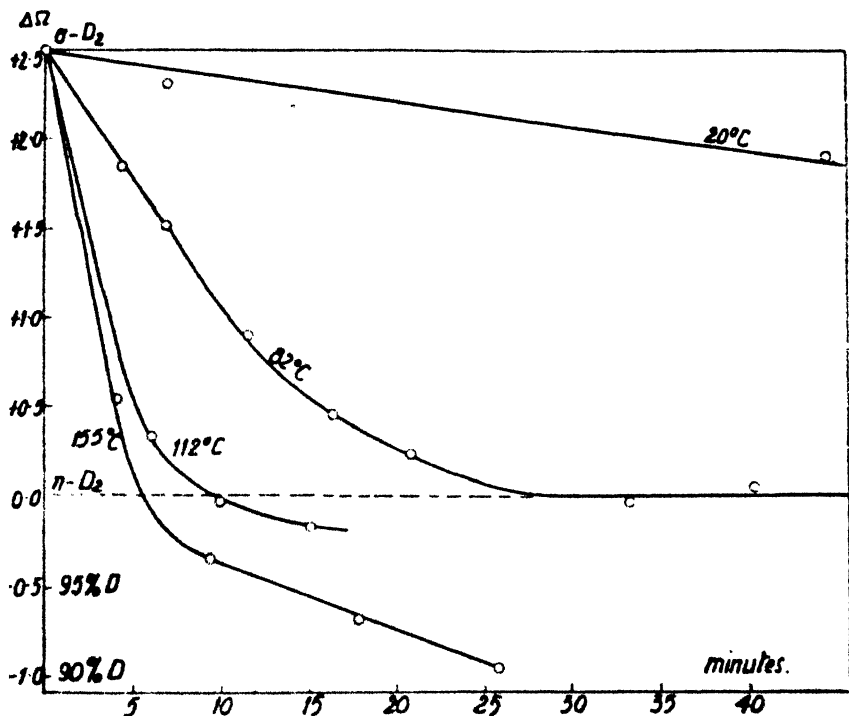


FIG. 8.

gas. Although it was not possible to analyse this gas owing to its small amount ($2 \cdot 10^{-4}$ c cm. N.T.P.) it was shown that it was formed from the ammonia and not displaced by it from the catalyst in the following way. A newly formed catalyst was brought into contact with deuterium, its activity being measured by the catalytic conversion of $o\text{-D}_2$. The gas formed by admitting NH_3 was mixed with sufficient (100 per cent.) D_2 in order to obtain $4 \cdot 10^{-3}$ c.cm. (N.T.P.) of gas which was the minimum amount necessary for one measurement in the thermo-conductivity cell. The D-content of this sample was found to be 96 per cent. showing that the gas formed was not deuterium displaced by the ammonia from the catalyst. In the thermo-conductivity cell the resistance values for H_2 and N_2 are approximately equal and therefore it was not possible to decide whether the defect of 4 per cent. D was due to the presence of H_2 alone or to a mixture of $\text{H}_2 + \text{N}_2$. The poisoning effect is shown in Table VIII.

TABLE VIII.

Treatment.	Pressure in mm. Hg.	Half-Life of the Conversion in Minutes.
Fresh catalyst	0.06	2
3 mm. NH ₃ added and removed . . .	0.06	11
Fresh catalyst	2	3.5
NH ₃ added and removed	2	13
Pumped for 45 minutes	2	22
NH ₃ added and removed	2	24

Discussion.

We assume that this reaction is taking place between molecules adsorbed on the surface of the catalyst. As far as the ammonia is concerned this assumption is justified by the strong adsorption which causes the inhibiting effect of the *para-ortho*-conversion and the independence of the rate of the exchange reaction on the ammonia pressure. On the other hand from previous experiments ^{9,10} we know that the *ortho-para*-interconversion likewise takes place in the adsorption layer, and from the following it will be seen that there is a connection between the conversion and the exchange reactions.

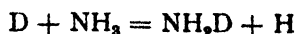
We can examine the following two reaction mechanisms ² making the further assumption that no transport processes between the gaseous phase and adsorption layer affect the actual reaction rate.

- Mechanism I. (a) $D_2 = D + D$
 (b) $D + NH_3 = (NH_3D) = NH_2D + H$
 (c) $H + D = HD.$
- Mechanism II. (a) $D_2 = D + D$
 (b) $NH_3 = NH_2 + H$
 (c) $NH_2 + D = NH_2D$
 (d) $H + D = HD.$

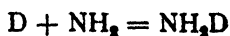
Mechanism I. is the heterogeneous analogue to the mechanism involved in the thermal interaction between NH₃ and D₂ occurring at 600° C. and upwards in the gaseous phase.⁷

In both mechanisms the activation of the deuterium is common. If the activation of the deuterium consists in dissociation (or at least in loosening the bond between the deuterium atoms) the *ortho-para*-conversion gives us a measure of this step since every dissociation and recombination process is necessarily connected with conversion. Actually it is found that the conversion reaction proceeds very much more quickly than the exchange reaction indicating clearly that II. (a) and (d) and I. (a) and (c) are not the rate determining steps. The dependence of the reaction rate on pressure suggests that neither is II. (b) rate determining since this reaction could not be accelerated by increasing D₂ pressure.

Thus we come to the conclusion that either the exchange reaction I. (b)



or the recombination reaction II. (c)



is the rate determining step depending whether mechanism I. or II. is valid. This is an interesting result since it shows that we have the same dependence of the rate of exchange on the pressure of NH_3 and D_2 (provided the ammonia is strongly adsorbed) whether ammonia is completely dissociated or not and that the kinetics of this reaction is compatible with both mechanisms.

Thus our problem reduces to enquiring how the ammonia is adsorbed.

Even at room temperatures a slight evolution of gas is observed when ammonia is brought into contact with a fresh iron surface. This cannot be due to a slow decomposition of ammonia into N_2 and H_2 since the formation of gas is only observed with a fresh catalyst and stops suddenly. It is more probably due to a reaction $NH_3 = NH_2 + H$ in which the radical NH_2 remains on the catalyst whereas the hydrogen is given up into the gas phase. This behaviour was actually observed by Frankenburger and Hodler,¹¹ who were able to show that on admitting ammonia to tungsten powder at 90° C. only hydrogen is evolved. It is also well known that at 500° C. nitride formation occurs which is not restricted to the surface of the iron but proceeds into the bulk phase. The formation of nitride and its reduction by hydrogen were demonstrated experimentally by Dünwald and Wagner.¹² Finally the experiments of Winter¹³ on the catalytic decomposition of ammonia on iron show definitely that the rate determining step is the decomposition of the nitride indicating that loosening of N—H bonds takes place before the nitride is decomposed.

The experimental evidence justifies the assumption that on the surface of the catalyst at 200° C. a large fraction of the ammonia is dissociated* and makes it probable that for the exchange reaction mechanism II. is responsible.

Thus we can form the following picture of the interaction of ammonia with deuterium (or hydrogen) on the catalyst.

In the absence of ammonia, hydrogen or deuterium are very easily dissociated on the catalyst as shown by the low activation energy for the conversion (8.9 kg. cal.). The conversion involves not only the dissociation process but also a migration of the hydrogen atoms since it is found that $H_2 + D_2 = 2HD$ reaction proceeds with a similar speed when compared with the conversion.†

If ammonia is added the greater part of the surface is covered cutting down the area accessible to hydrogen. At 20° C. a part of the ammonia covering the surface is decomposed into amide and hydrogen and the

¹¹ (a) Frankenburger and Hodler, *Trans. Faraday Soc.*, 1932, **28**, 229; (b) Frankenburger, *Z. Elektrochemie*, 1933, **39**, 45, 97, 269.

¹² Dünwald and Wagner, *Z. physik. Chem.*, 1934, **24B**, 53; Engelhardt and Wagner, *ibid.*, 1932, **18B**, 369.

¹³ Winter, *Z. physik. Chem.*, 1931, **13B**, 401.

* Whether the dissociation of ammonia proceeds according to $NH_3 \rightarrow NH + H_2$, $NH_3 \rightarrow NH + H$, $NH \rightarrow N + H$, and to what an extent these processes occur we cannot infer.

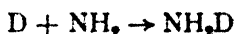
† It will be noticed, however, that the rate for the reaction $H_2 + D_2$ does not lie between that for the *ortho-para*-conversion of hydrogen and deuterium but is slower than either reactions. This effect (if not due to some impurity) might suggest that the migration involves a slightly larger energy of activation than the dissociation but in any case this difference is negligible being less than 1 k. cal.

hydrogen leaves the surface. The irreversibility of the inhibiting effect of ammonia is due either to a strong adsorption or to this surface amide formation, the hydrogen not being able to reduce the surface amide at these low temperatures. At higher temperatures (100° C.) the surface amide becomes reducible and the inhibition by ammonia becomes reversible. This reduction occurring according to



is the same reaction as the rate determining step in our mechanism II. of the exchange reaction. The actual exchange reaction however only becomes observable if the reduction proceeds with a very great speed as shown by the following example. Let us assume 1 cm.² of active surface in contact with 10²⁰ molecules of a mixture of D₂ and NH₃ (10²⁰ molecules are contained in 50 c.c. at 50 mm. Hg pressure). If the reduction of the 10¹⁵ molecules covering the surface of the catalyst takes place in one second the exchange reaction would require 10⁵ seconds. Thus the poisoning effect over this temperature range is due to the formation of the surface amide which also explains the fact why the *ortho-para*-conversion is not inhibited at higher pressures of ammonia. Through the dissociation process one part of the surface (namely that occupied originally by the third H-atom of the NH₃) remains always accessible to the hydrogen. A similar explanation might be advanced to explain the fact that no displacement of deuterium by ammonia is observed. (Cf. Tables IV. and V.)

Increasing the temperature (100° C. and upwards) the reduction of the amide occurs sufficiently rapidly and the exchange reaction appears. The activation energy for this exchange reaction is found to be 15 kg. cal. This is not the activation energy for the migration of hydrogen or deuterium which is much smaller namely 8 kg. cal.; it is more likely to be associated with the reaction



itself, whereas the back reaction, the dissociation, must have a smaller energy of activation not being the rate determining step. It is therefore most probable that the greatest part of this energy of activation is due to the exothermicity of the reaction $\text{NH}_3 \rightarrow \text{NH}_2 + \text{H}$.

The apparent energy of activation as calculated from the dependence of the reaction rate on temperature includes the heats of adsorption for the reactants. Owing to the strong adsorption of the ammonia we might assume that the adsorption layer is saturated with NH₃ over the whole temperature range and that therefore the heat of adsorption for NH₃ does not affect the true energy of activation. We do not know the exact heat of adsorption of D₂ but it will not be more than a few kg. cal. and therefore the true energy of activation will be somewhat larger than the apparent one. The concentration of deuterium will be rather low in the adsorption layer and this explains why the rate of exchange is approximately proportional to the square root of the deuterium pressure (Tables IV. and V.).

At still higher temperatures (over 300° C.) two new processes come into play, the decomposition of the surface nitride into molecular nitrogen and the migration of the nitride-N into catalyst the first reaction being responsible for the decomposition of ammonia, the second for the formation of iron nitride in bulk.

The author has great pleasure in expressing his indebtedness to Professor E. K. Rideal, F.R.S., for many discussions and his constant interest in this work. His thanks are also due to the Imperial Chemical Industries Ltd., for a grant.

Summary.

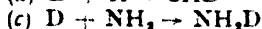
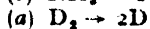
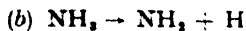
The exchange of hydrogen atoms between D_2 and NH_3 has been investigated on an iron catalyst at pressures of 30 to 400 mm. Hg and temperatures of 160° to 230° C.

The rate of the exchange reaction is independent of the ammonia pressure and increases with increasing D_2 pressure.

The apparent heat of activation is 15 kg cal.

The *ortho-para*-conversion of hydrogen and deuterium and the interaction $H_2 + D_2 = 2HD$ proceed much more quickly than the exchange reaction the activation for the conversion reactions being 8.9 kg cal. The *ortho-para*-conversion of hydrogen is inhibited by the presence of NH_3 .

It is suggested that the exchange reaction proceeds by the mechanism (all reactions occurring in the adsorption layer)



the step (c) being the slowest reaction and thus determining the rate. The reactions (a) and (d) are those involved in the conversion reactions. It is shown that this mechanism is in agreement with the experimental results.

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THE MECHANISM OF ELECTROLYTIC PROCESSES. PART I. THE ANODIC OXIDATION OF SOME METALS OF THE PLATINUM GROUP.

BY J. A. V. BUTLER AND G. DREVER.

Received 11th October, 1935.

In previous papers¹ the anodic polarisation of platinum electrodes has been studied in some detail and the observations made were interpreted as showing that, prior to the establishment of the oxygen over-voltage, an adsorbed layer of oxygen is formed on the surface of the electrode. No evidence was obtained of the formation of a definite platinum oxide similar to that which can easily be demonstrated at gold electrodes, which has been postulated by some investigators.² We have now examined the behaviour of the metals palladium, iridium and rhodium, and find that a similar phenomenon occurs in the initial stages of their anodic polarisation. Under certain circumstances the

¹ Butler and Armstrong, *Proc. Roy. Soc.*, 1932, 137A, 604; Armstrong, Himsworth and Butler, *ibid.*, 1933, 143A, 89.

² Cf. Bowden, *ibid.*, 1929, 125A, 446; Hoar, *ibid.*, 1933, 142A, 628.

formation of a distinguishable "oxide" can be demonstrated at palladium and rhodium electrodes, but in the case of iridium, like platinum, no such formation has been observed.

Experimental.

The experimental cell (Fig. 1) consisted of two cylindrical vessels connected through a tap D. This was normally kept closed and prevented products at the cathode C reaching the anode B. Connection with the

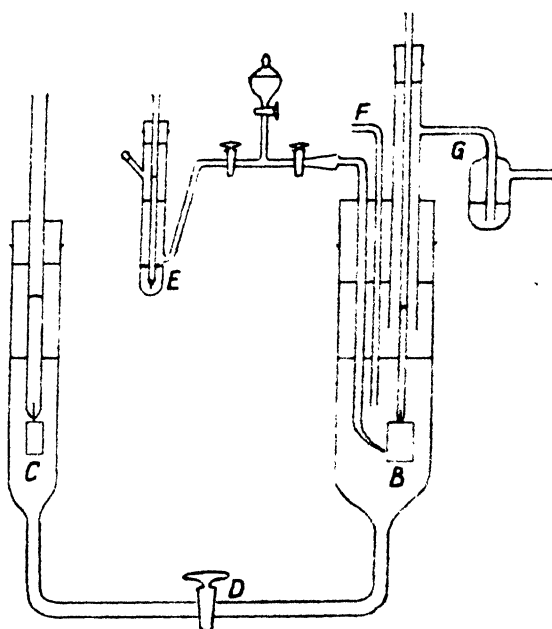


FIG. 1.—Electrolytic vessel.

standard electrode (E) was made with a fine tube, the end of which was almost in contact with the anode, so as to avoid the inclusion of the fall of potential in the electrolyte in the measured potential. The tubes F and G served to introduce oxygen-free nitrogen by means of which air was removed from the vessel.

The potential difference between the standard electrode and the anode was observed by means of a potentiometer in conjunction with a Lindemann electrometer, which enables rapid readings of variable potentials to be made. The electrode potentials have been reduced to the standard hydrogen scale. The

electrodes were made of foil supplied by Messrs. Johnson, Mathey & Co., and had a total apparent area of 1 cm.². Unless otherwise stated the experiments were carried out in an atmosphere of purified nitrogen.

The Adsorbed Oxygen Layer of Palladium, Rhodium and Iridium.

It has been found that if a platinum electrode is anodically polarised from a sufficiently negative value a comparatively slow linear change of potential occurs before the oxygen overvoltage is reached. The quantity of electricity passed in this process is of the same order as that required for the deposition of a single layer of oxygen atoms on the surface of the electrode, and it has been suggested that such an adsorbed layer is formed. This adsorbed layer is removed by cathodic polarisation to near the reversible hydrogen potential and the process can be repeated. But, if the anodic polarisation is begun at a more positive potential, such that the adsorbed layer previously formed has not been destroyed, the potential falls much more rapidly and the quantity of electricity then required (per volt) to change the potential is taken as a measure of the double layer capacity of the electrode in the absence of a depolarisation process.

Similar phenomena were observed with all three metals, and some

TABLE I.

Metal.	Apparent Area (cm. ²).	B Coulombs per 0.1 Volt.	Effective Area (cm. ²).	Coulombs Required for 1' O Atom per Metal Atom.	Coulombs passed in Linear Part of Anodic Curve.	Greatest Amount of Peroxide Formed Coulombs.
Pt	1.0	1.0×10^{-6}	3.0	16×10^{-4}	9×10^{-4}	—
Pd	1.0	1.8	5.4	29	30×10^{-4}	85×10^{-4}
Rh	1.0	1.2	3.6	19	9×10^{-4}	21×10^{-4}
Ir	1.0	2.0	6.0	32	22×10^{-4}	—

typical anodic curves taken after cathodic polarisation to near the reversible hydrogen potential, in dilute sulphuric acid, are shown in Fig. 2. Table I.

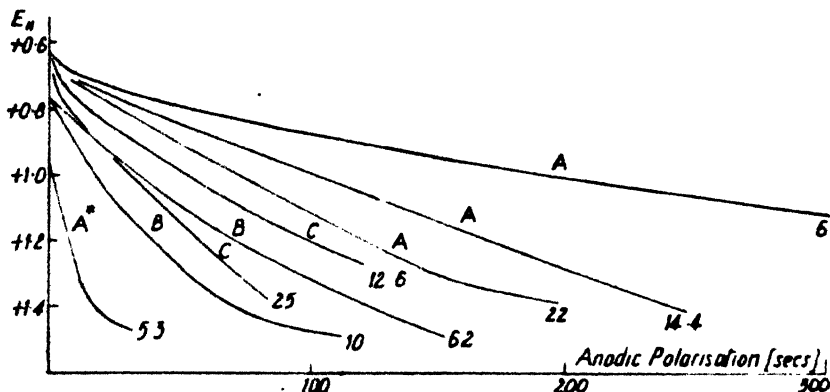


FIG. 2.—Anodic polarisation of (A) palladium, (B) Rhodium, (C) Iridium electrodes in dilute sulphuric acid (numbers represent currents in microamperes). A* is a "capacity" curve of palladium.

gives the quantities of current passed in the linear portions of these curves and the double layer capacities, B , which establish the real relative areas

It can be seen that the linear portion of the curve is in each case of the same order as that which is required for the deposition of a single layer of oxygen. In the case of platinum and rhodium it is appreciably smaller numerically, which may be due either to the difficulty of making an exact estimate of B , or to the intervention of the liberation of oxygen while the "adsorbed layer" is still incomplete.

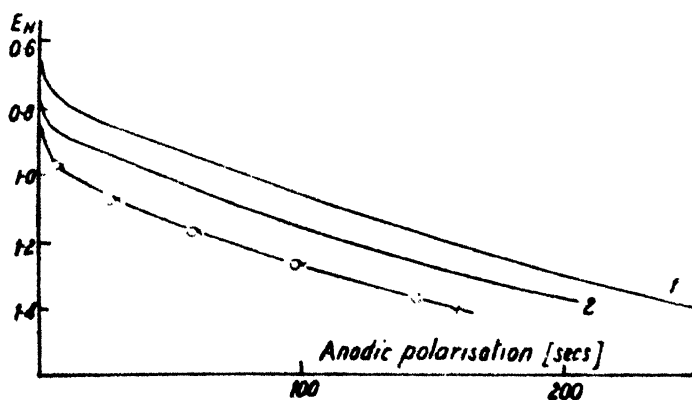


FIG. 3.—Effect of interval between the removal of the adsorbed oxygen and the anodic polarisation, with palladium electrode in presence of oxygen. Curve 1, anodic immediately after cathodic; curve 2, interval of two minutes; —x— interval of one hour; —○— interval of sixteen hours.

In order to see whether the adsorbed oxygen layer is formed at the surface of the metal on standing in contact with oxygen some experiments were carried out in which different intervals of time were allowed between the cathodic polarisation and the subsequent anodic, in solutions containing oxygen. Some curves obtained with palladium are shown in Fig. 3. After an interval the potential falls to a more positive value before the linear change, which has the same slope as before, occurs. The first part of the adsorption curve is thus missing, so that some adsorption of oxygen has taken place during the interval. This, however, does not proceed to the extent of the formation of a complete adsorbed layer even after a long interval.

The Formation of "Oxides" on the Electrodes.

After anodic polarisation the electrodes were cathodically polarised with a small current and the change of potential with the time was observed to see if any characteristic break occurs, such as has been observed with gold, representing the reduction of an oxide. With small anodic currents

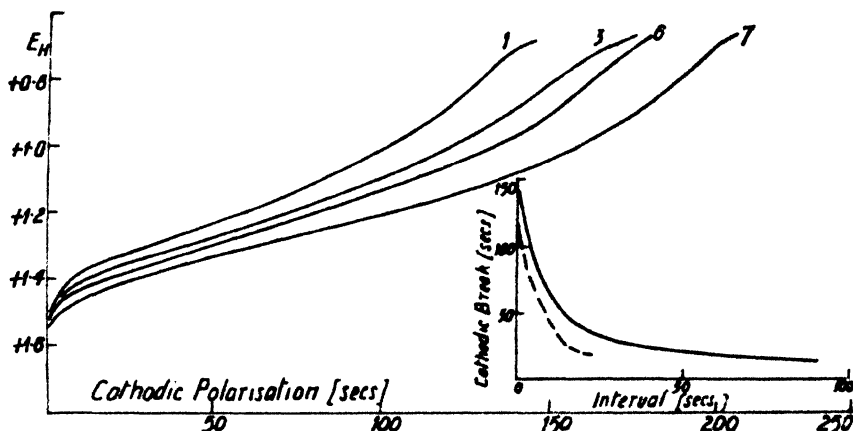


FIG. 4.—Cathodic curves of a palladium electrode after anodic polarisation in dilute sulphuric acid (Table II.). Inset, effect of interval on the length of the cathodic break (full line, unstirred; dashed line, stirred during interval).

the behaviour of all three metals was very similar to platinum, since only one depolarisation stage was observed in the cathodic curve which was clearly due to the reduction of the free oxygen liberated in the anodic process. It was observed that the decay at open circuit of the oxygen over-voltage was abnormally slow² with palladium electrodes, and this suggested the possible formation of traces of an oxide. It was then found that if the palladium electrodes were anodically polarised with much larger currents (of the order of 1 milli-ampere), a new depolarisation process occurred in the cathodic curve. Some examples of the cathodic curves obtained in dilute sulphuric acid are shown in Fig. 4. This process, which is clearly distinguished from the reduction of oxygen, since the latter occurs at a more negative potential, is interpreted as being due to the reduction of a superficial "oxide." The amount of oxide formed, as measured by the quantity of current required to take the potential to $E_H = +0.72$ volts, increases with the amount of anodic polarisation, but even after considerable anodic treatment it remains very small and in this case is cer-

² Cf. Armstrong and Butler, *Trans. Faraday Soc.*, 1933, **29**, 1261.

tainly less than a single molecular layer. A representative series of experiments is given in Table II.

TABLE II.—FORMATION OF "OXIDE" AT PALLADIUM ELECTRODES IN DILUTE SULPHURIC ACID.

Anodic Current, 700×10^{-6} amps.; Cathodic Current, 5×10^{-6} amps.

Experiment.	Anodic Coulombs.	Cathodic Coulombs to + 0.72.	Experiment.	Anodic Coulombs.	Cathodic Coulombs to + 0.72.
1	42×10^{-3}	7.0×10^{-4}	5	209×10^{-3}	8.3×10^{-4}
2	83	7.5	6	418	8.8
3	125	8.0	7	1255	10.0
4	167	8.2	—	—	—

If an interval is allowed between the anodic and the subsequent cathodic treatment, the length of the cathodic break is decreased and after about twenty minutes it has practically disappeared (Fig. 4, inset). Stirring the solution during the interval somewhat increases the rate of disappearance. The most probable interpretation of this behaviour is that the "oxide" has the properties of a peroxide, which decomposes spontaneously after the stoppage of the current. On this view its half-life period under these conditions is rather less than ten minutes.

The "peroxide" is, however, much more stable in dilute alkali, the decrease in the length of the reduction process being only about 8 per cent. in an interval of five minutes. Comparative experiments are thus more easily made in this solution. In experiments designed to ascertain the efficiency of the peroxide formation it was found that the amount formed was dependent on the previous history of the electrode. The oxidation occurs more readily at an electrode which has previously been oxidised and reduced than at an untreated electrode. This is illustrated by Table III., which shows a series of consecutive experiments in which the electrode was treated anodically first for increasing and then for decreasing times. Between each experiment the adsorbed layer was completely removed by cathodic polarisation.

TABLE III.—CONSECUTIVE EXPERIMENTS WITH A PALLADIUM ELECTRODE IN $N/5$ NaOH.

Anodic Current, 540×10^{-6} amps.

Experiment.	Anodic Coulombs.	Cathodic Coulombs to + 0.08.	Experiment.	Anodic Coulombs.	Cathodic Coulombs to + 0.08.
1	11×10^{-3}	5.3×10^{-4}	9	$2,600 \times 10^{-3}$	10.5×10^{-4}
2	22	5.6	10	4,900	16.7
3	32	5.9	11	11,000	33.7
4	65	6.2	12	20,500	43.5
5	130	6.7	13	320	18.6
6	194	7.0	14	160	17.2
7	550	7.6	15	30	13.1
8	1300	8.7	—	—	—

It can be seen that after long anodic polarisations a comparatively small amount of anodic treatment causes a much greater amount of oxidation than in the original state of the electrode. Since the adsorbed layer has been removed between successive experiments, the effect must be due to some change in the nature of the underlying metal which is produced

by the oxidation, but persists after the reduction of the oxide. The effect, however, disappears when the electrode is left untreated for a few days, for the electrode reverts to its original condition.

With larger currents of the order of 1 milliampere an appreciably greater amount of oxidation took place and a visible black film appeared on the anode.

TABLE IV.—OXIDATION OF PALLADIUM IN $N/5$ NaOH WITH 8.5×10^{-3} AMPS.

	Anodic Coulombs	Cathodic Coulombs		Anodic Coulombs	Cathodic Coulombs
(1)	510×10^{-3}	14×10^{-4}	(4)	$76,500 \times 10^{-3}$	85×10^{-4}
(2)	1020	19	(5)	1,020	70
(3)	5100	35	(6)	(8.4) *	48

* With $i = 28 \times 10^{-6}$.

It was again found that when the oxidation had once taken place, the oxide was reformed much more easily than initially. The final experiment shows that the oxidation can now be effected with small currents and that the efficiency of oxidation in the early stages is high. Even in the reduced state the electrode had lost its brightness, but after a few days' rest the brightness returned and the electrode reverted to its original condition.

Similar effects were observed with rhodium electrodes. No appreciable oxidation was at first observed with small anodic currents, but with large currents an additional depolarisation process similar to that of palladium appeared in the cathodic curve. The peroxide is not so stable as that of palladium for in dilute alkali ($N/5$) its amount decreased by about 15 per cent. in six minutes.

Like palladium, rhodium is rendered more susceptible to attack by previous anodic treatment. It was found that after oxidation with a large anodic current, even very small anodic currents, which were previously ineffective, were able to produce oxidation. It was therefore possible at such electrodes to observe the growth of the peroxide from the earliest stages of the anodic process. A current of 10.4×10^{-6} amps. was passed

TABLE V.

Experiment.	Potential Reached.	Coulombs $\times 10^{-4}$.			
		(1) Q_1	(2) Q_2	(3) $Q_1 - Q_2$	(4) Q_2
1	+ 0.18	3.1	1.5	1.6	1.5
3	+ 0.28	7.7	3.0	4.7	2.4
5	+ 0.38	9.9	4.5	5.4	3.7
7	+ 0.48	13.0	6.0	7.0	6.0
9	+ 0.58	18.2	7.5	10.7	9.2
11	+ 0.68	22.9	9.0	13.9	13.8
13	+ 0.78	30.5	9.0	27.5*	19.3

* The evolution of oxygen has begun at this point and this figure includes current employed in the liberation of oxygen.

tial to the given value, Q_2 the amount required at an untreated electrode in the normal formation of the adsorbed oxygen layer. The difference $Q_1 - Q_2$ is the amount which has presumably been employed in the formation of

anodically, taking the potential in successive experiments to increasingly positive values. After each such anodic polarisation the current was reversed and the amount of "oxide" measured by the quantity of current required to take the potential to -0.02 volts. The adsorbed oxygen layer was destroyed by further cathodic polarisation before the next anodic treatment. The results are shown in Table V. Q_1 is the total anodic polarisation required to take the poten-

the peroxide. Q_p is the amount of cathodic polarisation required to reduce the peroxide.

The figures in column (2) are based on the assumption that the amount of current required to produce the adsorbed layer is the same as in the original state of the electrode. That this is not far from true is shown by the approximate agreement of columns (3) and (4). Thus it is evident that at a previously oxidised electrode, the peroxide is formed simultaneously with the deposition of the adsorbed oxygen and at about the same rate. The formation of peroxide continues at a slow rate, however, after the evolution of oxygen has begun.

When the electrode is in this state, it is not possible to obtain either the normal anodic "capacity" curve, or the curve normally representing the formation of the adsorbed layer. Fig. 5 shows curves representing the anodic polarisation from two different potentials. Before curve A the electrode has been taken to near the reversible hydrogen potential, so as to destroy the adsorbed layer of oxygen. The anodic curve is flatter than the normal, the quantity of current passed being that required to deposit the adsorbed layer, with the concomitant "peroxidic" oxygen (*cf.* Table V.). Before curve B

the electrode has been polarised cathodically sufficiently to reduce the "peroxidic" oxygen but not to destroy the adsorbed layer. The quantity of current passed is thus that required to replace the peroxidic oxygen. The differences between the quantities of current required to reach

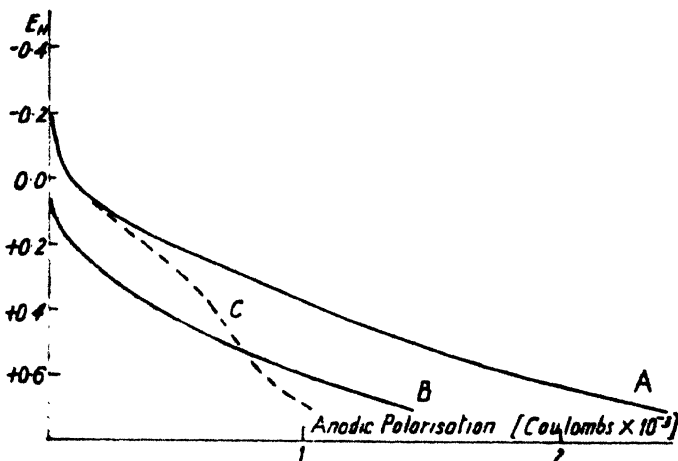


FIG. 5.—Anodic polarisation of a rhodium electrode in 0.2N NaOH.

various potentials in curves A and B, which are shown by curve C, should therefore represent the current used in forming the adsorbed layer. Since this corresponds fairly closely with that of a normal electrode, it appears on this ground also that the electrode area has not been much increased by the previous anodic treatment.

Similar experiments were made with iridium electrodes in dilute acid and alkaline solutions, but no evidence of peroxide formation was obtained. In the case of platinum no signs of this behaviour had been observed in the experiments previously recorded, and new experiments were made with comparatively large currents, but no oxidation was observed. However, it has been noticed,⁴ that the rate of decay of the overvoltage at open circuit is slower than the theoretical rate for the first 100 seconds after stopping the current. It was suggested that this was "due to a slight electromotive activity by the oxygen formed in the electrolysis, which remains for a time (about one minute) and then disappears." By analogy with the other metals this behaviour might reasonably be attributed to the formation of a small amount of peroxidic oxygen which decomposes in dilute sulphuric acid in less than 100 seconds.

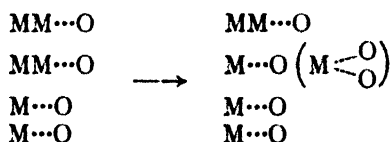
⁴ Armstrong and Butler, *loc. cit.*¹

Discussion.

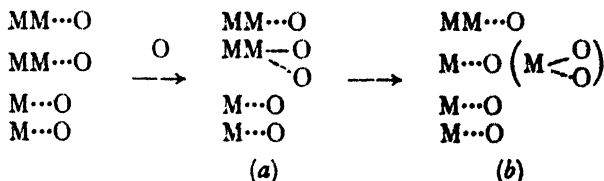
The formation of peroxidic layers has been demonstrated in the case of two of the four metals of the platinum group investigated. In the first place it is necessary, in view of the small quantities of oxide formed, to consider whether the effects might not be produced by the deposition of peroxides from traces of metallic impurities in the solution. If this were the case we should expect the electrodes of different metals to behave similarly and the phenomenon observed would be characteristic of the solutions rather than of the metals. To obtain conclusive evidence on this point a platinum and a palladium electrode were placed in the same solution and treated similarly. Peroxidation of the kind described occurred at palladium, but none was to be observed on the platinum.

The oxide is formed extremely slowly at a new electrode. In the case of rhodium the maximum amount observed is of the same order as a single molecular layer, while with palladium after very large amounts of anodic polarisation a layer of oxide several molecules deep is formed. When the oxide has once been formed, and reduced, it is very readily reformed.

Since the rate of oxidation is so small that it takes a considerable time to form even a single molecular layer of oxide, some parts of the surface must be more readily oxidised than others, and it must be supposed that the oxidation begins at exposed atoms or edges and spreads over the surface. This may be because the attachment of an exposed atom to the surface is so weakened by the attached oxygen that it is pulled out from the surface giving rise to a definite molecule of oxide, while the underlying metal atom now takes up an adsorbed oxygen, viz. :—



But since the oxidation occurs more rapidly with a greater current it is probable that the oxygen liberated is concerned in the formation of the oxide. This could happen if an exposed metal atom could take up a second oxygen atom as in (a), which will be "peroxidic" in character since it is more loosely held :—



The exposed atom is then pulled away from the surface, giving rise to a definite molecule of oxide as in (b), while an oxygen atom can then be adsorbed on the underlying metal atom. The stage (a) has not been directly observed, but indications of it are to be found in the slight electromotive activity which is observable at platinum after the stoppage of the current. This may be due to a slight peroxidation as in (a), without any distinguishable oxide formation.

The attack of an insoluble metal by oxygen at the anode thus takes place in the following stages. The formation of an adsorbed layer of oxygen is probably followed by the addition of peroxidic oxygen at exposed parts of the surface. With the more inert metals, platinum and iridium, the process stops here, but if the forces between the metal atoms are not so great the attachment of the "peroxidised" atoms to the surface may be so weakened that distinct molecules of the oxide are formed, and the neighbouring atoms are then left open to attack. This occurs very slowly with palladium and rhodium, more rapidly with gold and as will be shown in a further communication, very readily with the more easily oxidised metals, lead and nickel. When the surface oxide is reduced the atoms are probably redeposited in a chaotic condition and are readily reoxidised, but if the electrode is left standing for a few days a process akin to crystallisation takes place and the electrode reverts to its original inactive state.

It is unlikely that this phenomenon has any direct bearing on the oxygen overvoltage, for the rate of decomposition of the peroxide is not sufficient to make it a factor in the liberation of oxygen at the electrode, but it may have a secondary influence owing to the changes in the nature of the surface which are brought about. It has in fact been observed that in the continuous liberation of oxygen at a constant rate at these metals, the overvoltage continues to increase for some hours.

We thank Messrs. Imperial Chemical Industries and the Earl of Moray Endowment for grants for apparatus and materials respectively.

Summary.

1. When electrodes of palladium rhodium and iridium are anodically polarised in acid and alkaline solutions, an adsorbed layer of oxygen is formed prior to the establishment of the oxygen overvoltage, similar to that previously demonstrated in the case of platinum.

2. With palladium and rhodium a second stage in the oxidation has been observed, *viz.*, the slow formation of oxides of a peroxidic character, which are reduced cathodically at a more positive potential than the adsorbed oxygen. The conditions of formation of these oxides have been investigated, and a mechanism of the oxidation suggested.

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THE MECHANISM OF ELECTROLYTIC PROCESSES. PART II. THE ELECTROLYTIC OXIDATION OF SODIUM SULPHITE.

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Received 11th October, 1935.

In recent years considerable additions have been made to our knowledge of the conditions under which oxygen is liberated in electrolysis at the anode, and a stage has been reached at which it is appropriate to reconsider the mechanism of electrolytic oxidations. Bowden¹

¹ Bowden, *Proc. Roy. Soc.*, 1929, 126A, 107.

showed that Tafel's relation $i = ke^{-aV}$, where $a = 2F/RT$, is obeyed in the liberation of oxygen at the anode, and if Gurney's quantum mechanical interpretation³ of this relation is correct this implies that the discharge takes place by the transfer of electrons from (hydrated) hydroxyl ions near the electrode. It has, however, been shown³ that before the voltage necessary for the liberation of oxygen is reached, a layer of adsorbed oxygen atoms is formed on the electrode surface of platinum and other noble metals. In the case of palladium and rhodium⁴ a small amount of peroxidic oxide also is slowly deposited during the oxygen evolution. At the more easily oxidisable metals such as lead and nickel, oxides of a peroxidic nature are formed by anodic polarisation in appreciable quantities.

The possible processes by which an electrolytic oxidation may be effected may thus be listed as follows:—

A. A primary electrochemical oxidation by the direct transfer of electrons to the electrode from the substance in solution or adsorbed on the electrode surface.

B. A secondary oxidation brought about by a primary product of the electrolysis, such as:

- (1) Atomic oxygen liberated by the primary discharge of hydroxyl ions;
- (2) Adsorbed oxygen;
- (3) Any other primary product of the electrolysis, *e.g.*, superficial peroxides.

It is possible to distinguish between these processes to some extent by observing the electrode potentials at which the oxidation takes place. If the primary process is the liberation of free oxygen which effects the oxidation by a secondary reaction with the depolariser, the potential should be that at which oxygen is normally produced under the given circumstances. The adsorption of the depolariser on the electrode may cause displacement of the potential in this case, but since this reduces the effective surface of the electrode the displacement will be in the positive direction. Therefore if the oxidation occurs at a more negative potential than that at which oxygen is produced under the same conditions in the absence of the depolariser, the mechanism B1 is ruled out.

It will also be possible sometimes to distinguish other cases, *e.g.*, when the electrolytic oxidation takes place at a more negative potential than that at which the deposition of adsorbed oxygen begins a primary electrochemical process (A) is indicated. If the oxidation takes place in the same region as that in which adsorbed oxygen is formed, a distinction between processes A and B2 will sometimes be possible by observing the effect of varying the p_H of the solution.

In order to find a system suitable for quantitative study preliminary experiments were made with solutions of aniline, methyl alcohol and formaldehyde. The first gave rise to insoluble films on the electrode, the second appeared to be oxidised in two distinct stages, while formaldehyde easily gave rise to insoluble polymerisation products. Finally, the oxidation of sodium sulphite was chosen as a suitable reaction.

³ Gurney, *Roy. Proc. Soc.*, 1931, 134A, 137.

³ Butler, Armstrong and Himsworth, *ibid.*, 1933, 143A, 89.

⁴ Butler and Drever, this vol., p. 427.

This oxidation has already been extensively studied, the main products being sulphate and dithionate. Foerster and Friesner⁶ and Friesner⁶ found that the yield of dithionate was influenced by the nature and the previous treatment of the electrode and for this reason the latter rejected the simple electrochemical mechanism ($2\text{SO}_3^- = \text{S}_2\text{O}_6^- + 2e$) and suggested that the oxidation was effected by oxygen, *viz.* :—



Essin⁷ extended this view and suggested that no dithionate could be formed until a certain pressure of oxygen was reached, but Glasstone and Hickling⁸ have shown that this view is untenable since dithionate is formed as readily at less as at more positive potentials. The latter have re-examined the conditions and products of the oxidation and, in line with their general theory of electrolytic oxidation,⁹ suggest that the primary product which effects the oxidation is hydrogen peroxide. It is supposed that dithionate is formed by the action of hydrogen peroxide alone, while sulphate is produced both by hydrogen peroxide and its decomposition product, oxygen. Thus any circumstances which favour the decomposition of hydrogen peroxide should increase the yield of sulphate. It was found that the addition of substances (Mn^{++} , Co^{++} , Fe^{++} , powdered Ag) which are known to be catalysts for the decomposition of hydrogen peroxide decreases the yield of dithionate. Walker and Weiss¹⁰ have, however, pointed out that under the conditions of Glasstone and Hickling's experiments on the effect of catalysts on the Kolbe synthesis, oxidic films are frequently deposited on the electrode and the change in the nature of the electrode surface is quite capable of producing the variation of the oxidation products.

Experimental.

Procedure. The object of these experiments was to see whether the possible mechanisms of the oxidation could be distinguished by a study of the current-potential and time-potential curves. The classical method of determining current-potential curves, in which a definite voltage is applied to the cell and the final value of the current passing is observed, often fails to give information as to the initial stages of the electrolysis. In this work constant currents were employed and observations made of the potential of the electrode a definite time after starting the current. In many cases supplementary information was also obtained by observations of the potential with the time. The experiments were made on un-stirred solutions, since this has been found to be a convenient means of observing consecutive processes.

Sodium sulphite solutions in ordinary distilled water are fairly rapidly oxidised, owing probably to the catalytic influence of traces of copper. The water employed was redistilled in a Pyrex apparatus from barium hydroxide and potassium permanganate, and gave reasonably stable solutions, with which reproducible time-potential curves could be obtained.

The buffer solutions of p_H 6-8 were of $M/20$ KH_2PO_4 , with the appropriate additions of NaOH, while those of p_H 9-10 contained $M/20$ H_3BO_3 .

⁶ Foerster and Friesner, *Ber.*, 1902, **35**, 2515; *Z. physikal. Chem.*, 1904, **47**, 659.

⁷ Friesner, *Z. Electrochem.*, 1904, **10**, 265.

⁸ Essin, *ibid.*, 1928, **34**, 78.

⁹ Glasstone and Hickling, *J. Chem. Soc.*, 1933, **125**, 829.

¹⁰ *Ibid.*, 1932, **134**, 2345, 2800.

¹¹ Walker and Weiss, *Trans. Faraday Soc.*, 1935, **31**, 1011.

$M/20$ KCl with appropriate amounts of alkali. It was found by the use of indicators that the addition of $M/100$ Na_2SO_3 did not cause a significant change of the p_{H} of these solutions.

The electrodes were of platinum foil of 2 cm.² apparent area. When observing the variation of the potential with time, the electrode was prior to each experiment cathodically polarised to near the reversible hydrogen potential and the solution was then stirred by passing a stream of nitrogen for five minutes. When this procedure was carried out exactly reproducible curves were obtained. The current-potential curves, which show the potential reached a definite time after starting the current (fifty seconds) were obtained from the time-potential curves when the change of potential with time was appreciable. When the latter was small, the potential was observed at the stated interval. The apparatus was similar to that described in Part I.

The Current-Potential Curves of $N/100$ Na_2SO_3 in Solutions of Various p_{H} .

These curves, which are shown in Fig. 1, give a general picture of the conditions under which the oxidation takes place. It can be seen that

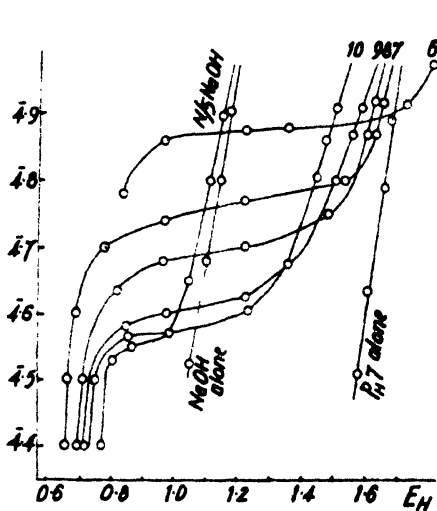


FIG. 1.—Current-potential curves for $N/100$ Na_2SO_3 in buffer solutions of various p_{H} .

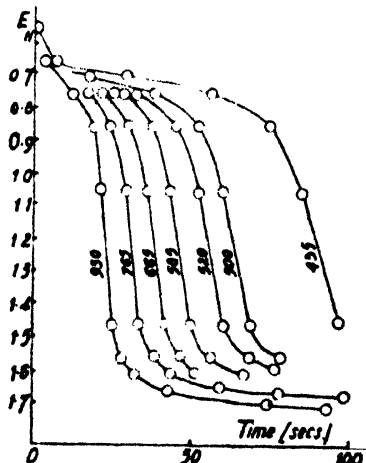


FIG. 2.—Time-potential curves for $N/100$ Na_2SO_3 in buffer p_{H} 7. The numbers on the curves refer to the current in amps $\times 10^{-4}$.

with small currents the electrolysis begins between $E_{\text{H}} = +0.65$ and $+0.75$, but as the current is increased a transition occurs and the potential falls to near the oxygen discharge potentials of the buffer solution. While the potential of the initial stage is not much affected by the p_{H} of the solution (it moves slightly towards the positive as the p_{H} increases), that of the final stage is considerably displaced in the negative direction by increase of p_{H} . The fall of the potential which occurs in the transition is thus small in alkaline solution and becomes greater as the acidity increases. The current at which the transition to the lower potential stage takes place increases as the p_{H} is decreased.

It has been found¹¹ that the transition current, when determined in this way, is approximately proportional to the concentration of the depolariser. The magnitude of the change observed is, however, comparatively small over a wide range of p_{H} , and it cannot be concluded that

¹¹ Butler and Armstrong, *Proc. Roy. Soc.*, 1932, 137A, 604.

the change is due to the relative concentrations of the HSO_3^- ion, which vary very much more widely in these solutions. Indeed we may conclude from the comparative independence of the potential of the initial stage, together with the small variation of the transition current that the process is not affected by the proportions of HSO_3^- and SO_3^{2-} present in the solution.

The Time-Potential Curves.

In order to find the cause of the transition observed above, the variation of the potential with time was observed in various solutions with currents in the neighbourhood of the transition current. A typical series obtained with $N/100$ Na_2SO_3 in a buffer solution of p_{H} 7 is shown in Fig. 2. Similar curves were obtained with other concentrations of sulphite. Defining the transition time t as the time in which the potential reaches + 1.2 volts, it is found that for each solution the relation

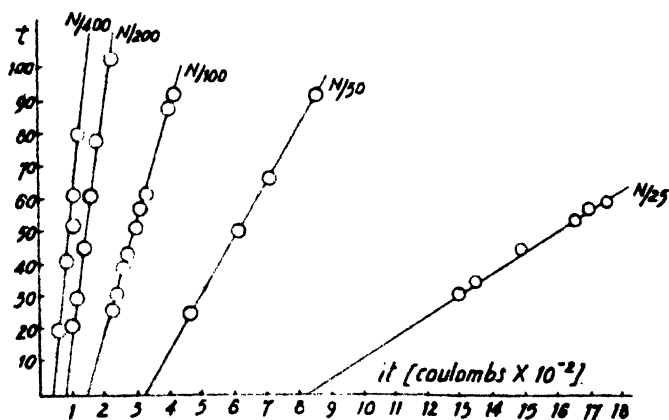


FIG. 3.—Effect of concentration of Na_2SO_3 (in buffer of p_{H} 7) on the length of the anodic break (t) to $E = 1.2$ volts.

it is found that for each solution the relation

$$it = i_0 t + \alpha$$

holds, where i is the current, and i_0 and α are constants. The graphs of it against t , which demonstrate this relation are shown in Fig. 3. The following table shows the values of i_0 and α for the various concentrations, and it can be seen that, except at the highest concentration, these constants are approximately proportional to the concentration. This relation has been obtained under similar conditions in a number of other electrochemical reactions¹² and has been interpreted in these cases as a consequence of the depletion of the depolariser near the electrode. i_0 represents the limiting current below which no transition occurs. When the current is smaller than this value, the depolariser can reach the surface by diffusion from the solution at a rate equal to or greater than that at which it is being removed; but when a greater current is employed the rate of removal of the depolariser by the electrochemical process is

CONSTANTS OF EQUATION $it = i_0 t + \alpha$ IN VARIOUS CONCENTRATIONS OF SODIUM SULPHITE.

C.	i_0 (Amps. $\times 10^{-6}$).	α (Coulombs $\times 10^{-2}$).
0.0025	65	0.4
0.005	125	0.8
0.01	290	1.5
0.02	570	3.3
0.04	1850	8.3

greater than the rate of diffusion and ultimately the supply of depolariser near the surface is exhausted, and the potential falls to a lower value at which an alternative process can take place. We may therefore conclude that the transition observed in this reaction is due to the same effect.

¹² *Loc. cit.*, (11) and (3).

The Nature of the Oxidation Process.

We have now to consider the nature of the process which occurs in the primary stage of the electrolysis. It is known that adsorbed oxygen is formed over a range of potentials more negative than that at which oxygen is liberated. This range has not been clearly defined, and experiments were made to define the region in the buffer solutions employed. The curves obtained in a buffer of p_H 7 are shown in Fig. 4*a*. The group A, of the anodic polarisation in the buffer solution containing no sulphite, shows the linear stage XY which indicates the deposition of adsorbed oxygen. The group B, of the same solution containing $N/100$ Na_2SO_3 , shows clearly that the electrolysis begins at a more negative potential than that at which the formation of adsorbed oxygen takes place. The electrolytic process taking place in this solution cannot be due to prior formation of adsorbed oxygen. On the other hand, in more alkaline solutions, the oxygen forming

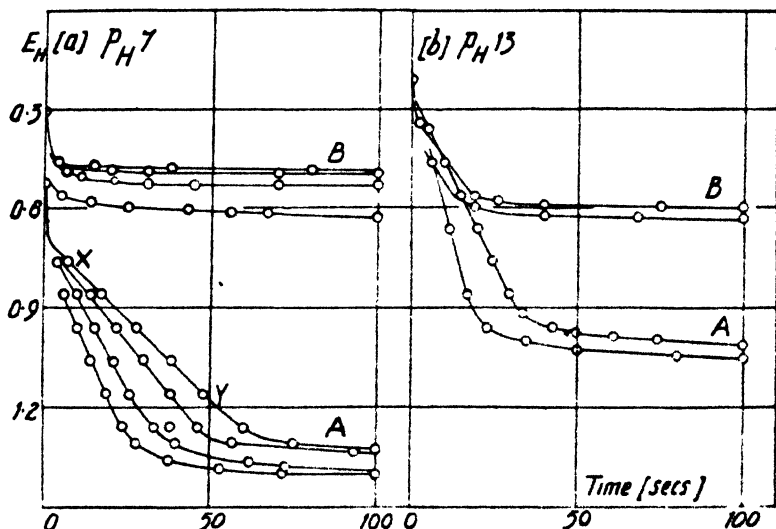


FIG. 4.—Time-potential curves of solutions (A) without and (B) with $N/100$ Na_2SO_3 . The currents with which the curves were obtained, taken in order downwards in amps. $\times 10^{-7}$ are: (a) Group A, 380, 470, 630, 830; Group B, 380, 470, 830, 2030; (b) Groups A and B, 420, 700.

processes move towards more negative potentials, while the potential at which oxidation takes place is comparatively unaffected. Thus it is found (Fig. 4*b*) that in alkali the oxidation occurs within the region in which adsorbed oxygen might be formed. In alkaline solutions it is therefore a possibility that the oxidation is effected by adsorbed oxygen, but it is very unlikely that the fundamental mechanism varies with the p_H .

Effect of Catalytic Substances.

Glasstone and Hickling¹³ found that the addition of salts of manganese, cobalt, iron, etc., caused a profound change in the course of the electrolytic oxidation. The yield of dithionate (except with cobalt additions) was markedly reduced and in the case of manganese the initial potential stage was nearly suppressed. They interpreted these changes in terms of their hydrogen peroxide theory, but Walker and Weiss have shown that in another oxidation process (Kolbe reaction) under the conditions of

¹³ *Loc. cit.*, (8), also *J. Chem. Soc.*, 1934, 136, 1878.

Glasstone's experiments visible films of "oxides" are frequently formed on the anode.

We examined the effect of small amounts of various salts on the time-potential curves under the conditions previously described. A phosphate buffer of p_H 7 was employed to which only small concentrations of the salt could be added without precipitation. Cobaltous, chromic and ferric salts at $M/5000$ caused small displacements of the initial stage in the positive direction, without having much effect on the transition time. The effect of manganese sulphate is shown in Fig. 5. It is observable even at $M/250,000$, and the initial potential stage is almost entirely suppressed at $M/2500$. In these more concentrated solutions a visible oxide film was formed on continued anodic polarisation and a study was therefore made of the conditions of its formation.

The Anodic Formation of MnO_2 Films.

In these experiments the solutions in the electrolysing cell were rigorously freed from oxygen by bubbling purified nitrogen for a considerable time. The nitrogen was purified by passing over red hot copper, followed by alkaline pyrogallol. The freedom of the solution from oxygen was shown by the absence of an oxygen break in the cathodic curve even when the solution was vigorously stirred.

It was found that manganese salts were precipitated in the phosphate buffers and in alkaline solutions at concentrations above $M/2500$, so that in order to use a greater concentration dilute sulphuric acid was employed as electrolyte in these experiments.

The conditions under which the film is formed are illustrated in Fig. 6, which shows the behaviour of $M/100$ $MnSO_4$ in $M/100$ H_2SO_4 . The anodic curve *abc* shows first the linear part *ab* along which the deposition of adsorbed oxygen occurs. In sulphuric acid alone this would continue to about +1.5 volts, but in the presence of the manganese the curve becomes horizontal (after a slight kink) at about +1.3. The cathodic curves were obtained by reversing the current after various periods of anodic polarisation. After seventy seconds anodic (which brings the potential to the point *b*) the cathodic curve shows a well-marked break *gh*, which is nearly equal in length to the linear stage *ab* and represents the removal of the adsorbed oxygen. After longer anodic polarisations it remains constant, but a new cathodic stage *df* appears, which is nearly equal to the length of the anodic treatment after the point *b*. This process is evidently the removal of the oxide film formed along *bc*. The oxide is thus formed and reduced at potentials only slightly removed from each other and the process of its formation and reduction is evidently reversible. The potential at which these processes occur is $E_H = +1.3$, which is in agreement with the recorded MnO_2/Mn^{++} potential¹⁴ for a solution of the same acidity, so that it can be concluded that the oxide deposited is MnO_2 .

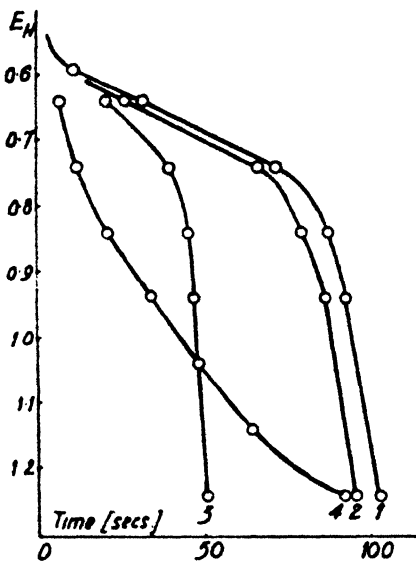


FIG. 5.—Effect of $MnSO_4$ on the time-potential curves of $N/100$ Na_2SO_3 in p_H 7; $i = 380 \times 10^{-6}$ amp. (1) No Mn; (2) $M/250,000$ Mn; (3) $M/10,000$ Mn; (4) $M/2500$ Mn.

¹⁴ Tower, *Sitz. Akad. Wiss., Wien* 1900, 32, 566; quoted in *I.C.T.*, vol. VI.

In some experiments with a larger anodic current (125×10^{-6} amps.), it was observed that signs of the film were just visible after the passage of 6×10^{-3} coulombs; it was a uniform pale yellow after 9×10^{-3} coulombs, pale brown after 19×10^{-3} coulombs and brown and opaque after 25×10^{-3} coulombs. The latter probably corresponds to a film of the order of 10 molecules deep. A similar series of colours appeared in the reverse order on removing the film cathodically.

The amount of cathodic treatment required to remove the film is usually slightly less than the quantity of electricity passed anodically in its formation. The difference is accounted for by the fact that the oxide dissolves spontaneously at a slow rate in $M/100$ sulphuric acid. The rate of solution is appreciably more rapid in $M/10$ and more concentrated solutions.

Taking this into account the oxide is deposited with 100 per cent. efficiency with small currents from $M/100$ MnSO_4 , but the efficiency of its formation becomes less when the concentration of manganese is reduced. Thus in $M/10,000$ MnSO_4 , the anodic potential does not remain constant

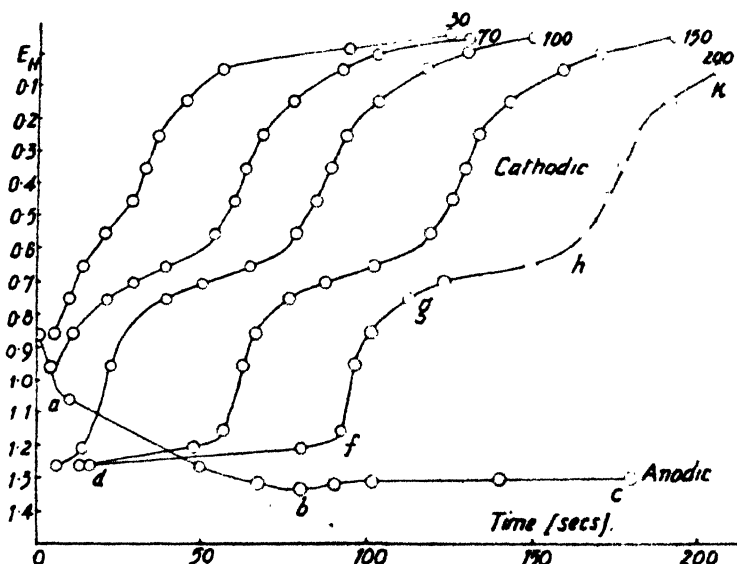


FIG. 6.—Formation and destruction of MnO_2 films; $i = 25 \times 10^{-6}$ amp. Numbers on cathodic curves refer to time of previous anodic.

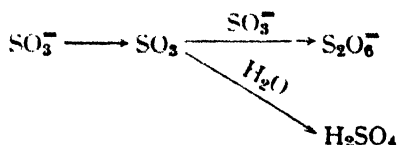
after the point *a*, but continues to fall slowly until the oxygen discharge potential is reached, and after 17×10^{-3} coulombs had been passed anodically the amount of oxide corresponded only to 3.5×10^{-3} coulombs.

The potential of the $\text{Mn}^{++}/\text{MnO}_2$ electrode is determined by the reaction $\text{Mn}^{++} + 2\text{H}_2\text{O} = \text{MnO}_2 + 4\text{H}^+ + 2e$, i.e., $E = E^\circ + 2RT/F \log (\text{H}^+)$, and thus for a constant concentration of Mn^{++} becomes more negative by 0.12 volts for each unit increase of p_{H} . The effect of the p_{H} on the deposition of MnO_2 is thus twice that on the discharge of oxygen and while in an acid solution the deposition of the oxide begins only when the adsorbed layer of oxygen is nearly completed, in solutions having a p_{H} greater than 7 the oxide is formed *before* the deposition of adsorbed oxygen. Thus in these solutions the deposition of the oxide takes place in the same region as that in which the primary oxidation of sulphite takes place, so that the suppression of the primary stage in the presence of manganese ions can be accounted for as due to the formation of a film of oxide, which may in the early stages of its formation at any rate be quite invisible. Presumably the primary oxidation process cannot take place at an electrode covered with MnO_2 .

Discussion.

It has been shown that in p_H 7 solutions the primary electrolytic oxidation takes place at a more negative potential than that at which adsorbed oxygen is formed, and indeed in a region in which no electrochemical process can be detected in the buffer solution alone. It is difficult to avoid the conclusion, contrary to that of previous investigators, that in this solution the oxidation is a primary electrochemical process brought about by the direct transfer of electrons from sulphite ions to the electrode. In more alkaline solutions ($p_H > 9$) the region in which adsorbed oxygen is formed overlaps the potential at which the oxidation takes place and reaction between adsorbed oxygen and the sulphite is clearly a possibility. Since, however, the oxidation potential is only slightly affected by changes of p_H it may be concluded that the primary oxidation process continues to take place even in the more alkaline solutions.

In these experiments the quantities of electricity passed are very small and it is not feasible to examine the products of the reaction. Glasstone and Hickling have shown, however, that dithionate and sulphate are the main products, the yield of the former being less than a half of the total oxidation. The simplest way in which these substances could be formed by a primary process is as follows: if a sulphite ion SO_3^- loses two electrons to the electrode, the uncharged SO_3 molecule may combine either with another sulphite ion or with water, *viz.*,



Similar processes are possible with the HSO_3^- ion.

It might be expected on this view that the yield of dithionate would be increased by an increase of the sulphite concentration, since the chance of the first reaction would be greater. According to Glasstone and Hickling's observations this is not the case. This difficulty would, however, occur in almost any theory of the reaction, since the dithionate must be formed from two sulphite residues. A possible reason is that the reaction takes place entirely between adsorbed materials and if the surface is practically saturated over the range of concentrations studied this effect would not occur.

In solutions of $p_H > 9$ another reaction is possible, *viz.*, $SO_3^- + O = SO_4^{2-}$, which will increase the proportion of sulphate formed. Since the amount of adsorbed oxygen formed at a given potential increases with increase of alkalinity, this reaction will also occur to a greater extent. This explains Glasstone and Hickling's observation that the yield of dithionate is a maximum in the region p_H 7 to 9 and decreases as the solution becomes more alkaline. They also found that the yield decreased in more acid solutions and became very small at p_H 1. While we have made no experiments in this region, it may be suggested as a possible explanation that undissociated H_2SO_3 and SO_2 , which are largely present in the more acid solutions, are unable to bring about the dithionate reaction.

Glasstone and Hickling also observed a transition from a higher to a lower potential during the course of the oxidation, under the conditions of their experiments, *viz.*, long continued electrolysis with a

rotating electrode. It is difficult to judge the significance of this. Transition phenomena due to the depletion of the depolariser also occur in stirred solutions, the effect of stirring being to decrease the thickness of the diffusion layer and so increase the transition time. However, many samples of distilled water contain slight traces of metallic impurity in amounts quite sufficient to form films of oxide a few molecules thick on the electrode, and a possible cause of the transition is the formation of such films in the course of a long continued electrolysis.*

In conclusion, we may observe that Glasstone and Hickling's arguments in favour of their hydrogen peroxide theory of electrolytic oxidation are almost entirely indirect, since it has not been shown that H_2O_2 is a product of the electrolysis under the conditions of the experiments. The more important indirect arguments on which they rely are (1) the transition of the potential has no significant effect on the yield of dithionate; (2) the yield of dithionate is a maximum at p_H 8 and decreases both in more acid and in more alkaline solutions, (3) the addition of substances which are catalysts for the hydrogen peroxide decomposition decreases the yield of dithionate. The first appears to be not clearly shown by Glasstone and Hickling's own curve, while it has been shown that the effect of changes of p_H can be alternatively explained. Finally the effect of catalytic ions can be attributed to the formation on the electrodes of peroxidic oxides at which the primary oxidation cannot take place.

Summary.

1. The conditions under which the electrolytic oxidation of sodium sulphite occurs in buffer solutions of various p_H has been examined.
2. It is shown that in $p_H = 7$ the oxidation takes place at a more negative potential than that at which adsorbed oxygen is formed. Since no other primary process is observed in this region with the buffer solution alone, it is concluded that the oxidation takes place in this solution by the direct transfer of electrons from the sulphite ions to the electrode. In solutions of $p_H = 9$ the oxidation occurs in the same region as that in which adsorbed oxygen is formed so that in these solutions oxidation by adsorbed oxygen is a possibility.
3. The effect of various added salts was studied and it was found that in the case of manganous salts, which are much the most effective, the suppression of the initial stage of the electrolysis was due to the formation of a film of manganese dioxide.
4. The results of this investigation are not in accordance with Glasstone and Hickling's hydrogen peroxide theory. An alternative mechanism has been suggested.

We acknowledge gratefully a grant made to W. M. L. by the Ritchie Bequest.

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* Glasstone and Hickling regard the changes of potential which occur as secondary effects produced by the accumulation of oxygen at the electrode and suggest that the oxidation processes themselves are not affected by the potential change since the curves showing the total oxidation and the amount of dithionate formed show "no marked discontinuity." It may be observed, however, their curves show that the efficiency of dithionate formation does in fact decrease as the electrolysis is continued and is much smaller at the end than at the beginning. The analytical accuracy is probably insufficient to show if a change of slope is associated with the potential transition.

THIXOTROPY AND RHEOPEXY OF V_2O_5 -SOLS.

BY F. JULIUSBURGER AND A. PIRQUET.

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I.

In a previous paper¹ there was described and briefly discussed a phenomenon found in some thixotropic systems which contain particles of strongly anisometric shape, *e.g.*, plate- or rod-like particles. Thixotropic sols (of V_2O_5) or suspensions (of gypsum) having a certain time of solidification, when left to themselves, could be solidified in a very much shorter time by moving the liquid in a gentle and regular way; for instance, by rolling the test tube containing the sample to and fro between the palms of the hands. This new effect was named "rheopexy."

It was there assumed that the cause of this solidification is the orientation of the particles brought about by the movement of the liquid. If this were true, one would expect that other means of orienting the particles, for instance a magnetic field or an electric current, would favour solidification in these thixotropic sols. Preliminary experiments in this direction have so far not been successful. This and other facts leave it an open question, whether orientation of the particles is really the cause of, or only a phenomenon accompanying the rheopectic behaviour.

The following paper deals mainly with another question: how is rheopexy related to ordinary thixotropy?

Practically all experiments were done with V_2O_5 sol. It showed valuable properties in many respects, although its lack of stability under certain conditions was a distinct drawback.

The experiments were performed in test tubes with ground-in glass stoppers having an inner diameter of 9 mm. Whether a sample had solidified or not, was tested by reversing the test tube carefully. Only when the gel did not flow at all, was it considered to be solid. The time, from the moment the gel had been fluidified by shaking till it had solidified, is referred to as the time of solidification θ . By spontaneous solidification is understood the transformation of a sol into a gel, when the sample is left to itself without being moved or disturbed. This is the ordinary thixotropic solidification. It must be distinguished from the rheopectic solidification caused by a suitable movement.

It has been found convenient to construct a special "machine" in order to produce in a better defined and reproducible way the to and fro movement of the test tube which has proved useful for solidifying rheopectic sols. The principle is very simple. A disc is rotated by a motor. By a suitable transmission this rotation is transformed into a movement to and fro of a pulley. The latter bears a cylinder containing the test tube with the sample.

The speed of the machine could be varied and the influence of this variation was studied in order to find the speed which would cause the

¹ Freundlich and Juliusburger, *Trans. Faraday Soc.*, 1935, 31, 920.

quickest solidification of any given sample. A speed of about 120 to 140 changes per minute was found to be the most favourable in the majority of experiments. If the speed was too small, the movement of the liquid was not sufficiently strong and a longer time was needed to cause solidification. This was also the case, if the tube was moving too fast, probably because too strong a movement destroys the structure already formed. When dealing with a very viscous sol, the best working conditions were at a higher speed. In the majority of cases, however, the properties of the various samples justified keeping the machine at the speed mentioned, without change.

Another kind of regular movement was also most suitable for causing rheopectic solidification: instead of rolling the test tube one can tap it gently and regularly on the table, holding it in a vertical position. It is advisable to cover the board with a sheet of filter paper. Obviously any vibration may cause rheopectic solidification. With the rheopectic suspension of gypsum in water, mentioned in the previous paper, a weak action of ultrasonic waves can cause rheopectic solidification. This experiment was not so successful so far with the much more sensitive V_2O_5 sols.

II.

In the paper mentioned the V_2O_5 sol showing rheopepy was about ten years old. Hence it was of interest to compare the properties of this sol, as to thixotropy and rheopepy, with those of a freshly prepared V_2O_5 sol.

In the following experiments frequent references will be made to sol A, B, and C.

Sol A was a V_2O_5 -sol which had aged about ten years. The amount of V_2O_5 , found by evaporating and melting for a very short time, was 0.16 per cent. The sol was reddish brown in reflected, clear red in transmitted light. When stirred and viewed in reflected light distinct streaks were seen abundantly.²

Sol B was a freshly prepared V_2O_5 sol which had aged for 3 weeks at the start, and for 7 weeks at the end of the experiments. As with sol A the method of preparation was that given by Biltz.³ The sol was dialysed in cellophane bags, which proved very suitable for this purpose. Dialysis went on for 3 weeks, the water being changed frequently. The appearance and properties of the dialysed sol differed markedly from those of the undialysed sample. The former evidently contained extremely small particles. The colour was almost black in reflected light, and deep red in transmitted light. The sol contained 0.72 V_2O_5 . For the sake of comparison, however, the sol was in some experiments diluted to the same concentration (0.16 per cent.) as sol A. Streaks were visible, when the sol was stirred, but they were much less pronounced than with sol A.

Sol C was prepared from sol B in the following manner: samples of sol B, contained in sealed test tubes, were heated in a water bath for about 47 hours. Care was taken not to expose the whole test tube to heating, for the reason that, if this were done, a part of the sol was destroyed, a coagulated deposit of V_2O_5 being formed at the boundary sol/water vapour/glass. But if the boundary sol/water vapour was cooled from outside, thus maintaining convection currents within the sol, a decomposition of the sol could easily be avoided. Heating has a very strong effect: sol C finally resembles sol A, as to colour and distinctness of streaks. An exposure to higher temperature evidently causes, in a much shorter time, practically the same changes as ageing at room temperature does in a considerably longer time. Sol C had the same concentration of V_2O_5 (0.72 per cent.) as sol B from which it had been prepared.

² Diesselhorst, Freundlich and Leonhardt, *Elster-Geitel-Festschrift*, 1915, p. 453.

³ W. Biltz, *Ber.*, 1904, **37**, 1098.

The thixotropic and rheopectic behaviour of these three sols was compared with their appearance under the ultramicroscope. Thus the influence of particle size upon thixotropy and rheopecty was examined.

We never succeeded in producing rheopecty with any sample of sol B; the time of solidification θ was the same, whether the sol, after being vigorously shaken, was left to itself or was rotated on the machine. In one experiment θ was in both cases 25 minutes (the sol contained 0.35 per cent. V_2O_5 and 39 m. Mol. $H_2SO_4/2$, the acid having been added at once).

Sol B, the freshly prepared sol, was undoubtedly strongly thixotropic, when a suitable amount of H_2SO_4 had been added, although it is not rheopectic. Under the ultramicroscope it was found to be optically void; only a Tyndall cone could be seen, but no single particles. This may be attributed entirely to the small size of the particles. For the difference in the refractive indices of V_2O_5 and the surrounding aqueous solution is great and quite sufficient to allow visibility. Nevertheless sol B shows a distinct optical anisotropy: streaks appear, when it is stirred; a sign that the particles are anisometric.

Sols A and C were both thixotropic and rheopectic. In sol A θ was, for example, 3 hours for the thixotropic, 8 minutes for the rheopectic change (the sol contained 0.15 per cent. V_2O_5 and 48 m. Mol. $H_2SO_4/2$; the acid was added at once). In sol C θ was 20 minutes for the thixotropic, 1 minute for the rheopectic change (the sol contained 0.23 per cent. V_2O_5 and 42 m. Mol. $H_2SO_4/2$; the acid was added in 11 equal portions).

Under the ultramicroscope both sol A and C were found to contain long, needle-shaped particles with a length up to about 10μ and more.⁴ In sol A particle size seemed to vary only slightly, whereas sol C appeared to be somewhat heterodisperse. In the latter there also were seen a number of particles which were considerably thicker than the majority of particles in this sol and in sol A, resulting probably from the somewhat crude procedure of preparing sol C from B. So long as no electrolyte was added, the needles showed Brownian movement. Most of them were so thin that they disappeared, when their long axis turned into a position parallel to the incident beam of light; they were obviously amiconic as to their two other dimensions.

When electrolyte was added in such an amount that it did not cause macroscopically visible coagulation, the Brownian movement gradually diminished until it ceased completely. The needles then seemed to form a kind of irregular structure. These ultramicroscopic experiments were

TABLE I.—SOL C.

The sol contained 0.23 per cent. V_2O_5 and 42 m. Mol. $H_2SO_4/2$. The acid was added in 11 equal portions.

t.	θ .	
	Thixotropic.	Rheopectic.
Immediately after mixing	20 min.	1 min.
7 days	much more than 1 hour	4 mins.
14 days	3½ hours	12 mins.
42 days	more than 1 hour	10 mins.

V_2O_5 sols containing H_2SO_4 are very unstable: the time of solidification, for instance, changes strongly in course of time. This made it desirable to investigate more

⁴ Good photographs of such needles have been published by Geasner, *Kolloid-chem. Beihft.*, 1924, 19, 213.

thoroughly the influence of varied conditions as to rheopexy and thixotropy.

The first impression, that both thixotropic and rheoplectic behaviour were limited to a very narrow range of V_2O_5 concentrations, did not prove to be correct. Sol A could be diluted to half its original concentration whilst remaining thixotropic and rheoplectic.

The change in course of the time t of θ of a rheoplectic and thixotropic sol is shown in a typical experiment (Table I.).

Table II. shows the influence of varying the concentration of electrolyte ; t is the time elapsed after mixing.

TABLE II.—SOL A (0.15 PER CENT. V_2O_5).

Amount of H ₂ SO ₄ /2 Present.	39 m. Mol.		48 m. Mol.		57 m. Mol.	
t.	θ.					
	Thixotropic.	Rheoplectic.	Thixotropic.	Rheoplectic.	Thixotropic.	Rheoplectic.
1 hour	still liquid	after 30 mins. still liquid	still liquid	2½ mins.	1 hour	1½ mins.
21 hours	more than 18 hours	30 mins.	more than 18 hours	20 mins.	45 mins.	3½ mins.
45 hours	liquid at least 24 hours	more than 20 mins.	more than 24 hours	15 mins.	several hours	4½ mins.
117 hours	liquid at least 60 hours	1½ hours	—	12 mins.	—	10 mins.

The influence of electrolyte concentration is marked and not simple. It is also important to add the electrolyte always in the same way in order to obtain the same results. The coagulation of sols is likewise often very sensitive to the rate at which the electrolyte is added. Obviously the same holds for thixotropy and rheopexy, which may both be considered as special, primary, stages of coagulation.

TABLE III.—THE SOLS CONTAINED 0.16 PER CENT. V_2O_5 AND 125 m. MOL. LiCl (90 m. Mol. being added at once, the rest after 20 hours.)

	Sol A.		Sol C.	
<i>t.</i>	θ .			
	Thixotropic.	Rheoplectic.	Thixotropic.	Rheoplectic.
20 hours	2 hours	8 mins.	2½ hours	2 mins.
5 days	approx. 2 hours	2 mins.	more than 2 hours	1½ mins.
33 days	12 mins.	30 secs.	22 mins.	45 secs.

The changes going on in course of time in these mixtures containing electrolytes also makes matters more complicated. One is probably dealing not only with changes caused by colloidal processes, but also with

the effects of chemical reactions. V_2O_5 is known to form complex compounds with many acids⁸ (notably H_2SO_4 , H_3PO_4 , H_3AsO_4 , etc.); these compounds are highly soluble in water and hygroscopic. This, at least in part, most likely accounts for the instability of rheopectic V_2O_5 sols containing H_2SO_4 .

Other electrolytes than acids, for instance LiCl, seem to behave in a more simple fashion as to the influence of the time t (cf. Table III.). This is probably due to the fact that presumably no chemical change takes place. But with LiCl, also, the rheopectic mixtures are not indefinitely stable; they coagulate in the course of one or two months.

III.

Previous attempts to use other electrolytes than acids for preparing rheopectic V_2O_5 sols had failed. This was somewhat surprising. For it is known that thixotropic V_2O_5 sols can be produced with various electrolytes, e.g., LiBr, NaCl, KCl, etc.⁹ Here we have obviously another point of difference between thixotropy and rheopecty which needs explanation.

Now it is also known that KCl is not specially suitable for making stable thixotropic V_2O_5 sols⁹; the proper range of electrolyte concentration is very narrow indeed and thixotropic sols prepared with KCl are coagulated in the majority of cases after 2 or 3 sol-gel transformations. Li-salts are definitely better: the range of electrolyte concentrations is broader, the thixotropic changes occur at higher electrolyte concentrations and generally need a longer time. The experiments, mentioned above, show that Li salts obviously favour both rheopectic and thixotropic solidification.

To find Li salts behaving in the same way as acids in acting upon a negative sol is extraordinary for, with most negative sols, the behaviour of Li salts is opposite to that of acids: Li salts being weaker coagulants than monovalent cations such as K^+ , NH_4^+ ion, etc., whereas H^+ ion is generally a much stronger coagulant than these cations.⁷ It has, however so far not been realised that V_2O_5 sols belong to those very few cases where acids are very weak coagulants.⁸ The other well-known case of this kind is Odén's sulphur sol,⁹ which always contains pentathionic acid.¹⁰ The table

TABLE IV. —COAGULATION VALUES.

Electrolyte.	Sol A.	Sol B.	Sol C.
LiCl	160	160	120
Li_2SO_4 2	120	120	120
KCl	2.8	7.0	2.1
K_2SO_4 2	8	12	8
$(NH_4)_2SO_4$ 2	very similar to K_2SO_4		
HCl	29	29	29
HNO_3	28	28	28
$HClO_4$	27	36(?)	27
H_2SO_4 2	44	dissolution	33
		no coagulation	
H_3PO_4 3	400	dissolution	310
		no coagulation	
H_3AsO_4 3	no coagulation, strong dissolution		
CH_3COOH		no effect	

of coagulation values (Table IV.) proves the truth of this assertion: the acids have indeed up to 10 times larger coagulation values than the K salts, and the Li salts still about 5 times higher ones.

⁸ Cf. for instance, H. Gmelin, 3, II., 1908, p. 109 *et seq.*; Ephraim, *Textbook of Inorganic Chemistry*, London, 1934, p. 434 *et seq.*

⁹ Kabinerson, *Kolloid-Z.*, 1934, 68, 305.

⁷ Cf. for instance, Freundlich, *Colloid and Capillary Chemistry*, p. 420.

⁸ Ostermann (*Wissenschaft u. Industrie*, 1922, 1, 17) has investigated the coagulation of V_2O_5 sols by HCl; he did not determine coagulation values, but was mainly interested in the ultramicroscopic behaviour of the process.

⁹ Odén, *Nov. act. reg. soc. scient. Upsal.*, 1913, Ser. IV., 3, Nr. 4.

¹⁰ Freundlich and Scholz, *Kolloidchem. Beih.*, 1922, 16, 234.

The experiments were carried out in the usual manner with a V_2O_5 sol having a concentration of 0.16 per cent. 0.5 c.c. of the sol were added to 0.5 c.c. of the electrolyte solution and thoroughly mixed. After waiting for 2 hours observations were taken. The minimum values to cause turbidity are given in terms of the concentration of the electrolyte (m. Mols./litre) present after addition of the sol; the latter then contained 0.08 per cent. V_2O_5 . The three sols do not differ much as to coagulation values. The chemical action of the acids, their ability to dissolve V_2O_5 , is specially pronounced in sol B, which contains by far the smallest particles; this was to be expected.

It is interesting to compare the coagulating values of the electrolytes in Table IV. with their respective ability to produce rheopexy. No rheopexy could be obtained with KCl, K_2SO_4 , $(NH_4)_2SO_4$. They had a strongly coagulating effect and within a narrow range of concentration thixotropic sols could be produced, when working very carefully. Acetic acid had no effect whatever upon sol A; it probably does not behave as a typical electrolyte. The behaviour of the other acids is remarkable. Rheopexy could be obtained with mono- and divalent acids, the suitable concentrations being the same as with H_2SO_4 . Samples made up with monobasic acids, however, appear to be less stable than those containing H_2SO_4 ; in some cases they were found to coagulate irreversibly after a few sol-gel transformations. As was mentioned above, the actions of acids is not merely due to coagulation; they also act chemically, dissolving V_2O_5 and forming complex compounds. With tribasic acids the chemical action outweighs any coagulating effect, so as to make it sometimes difficult to determine the latter at all. Li salts were specially suitable for preparing rheoplectic sols.

IV.

It results from the preceding paragraph that only those electrolytes give rheoplectic sols which are weak coagulants. One cannot replace them by strongly coagulating electrolytes using a correspondingly smaller concentration. This seems to show that it is a special property of the weakly coagulating electrolytes which makes them capable of producing rheopexy. The main point is perhaps that these electrolytes are able to coat the V_2O_5 particles with a strongly hydrated layer. With Li^+ ion such an effect would be evident: it is certainly a strongly hydrated cation and is markedly adsorbed by the negatively charged V_2O_5 particles. Not quite so obvious is the behaviour of the acids. It may most likely be attributed to the formation of complex compounds with V_2O_5 . The latter are very soluble in water and hence may be considered as having a strong affinity to water. When these compounds are formed on the surface of the particles, they produce there a highly hydrated layer.¹¹

A V_2O_5 sol containing a small amount of the complex compound formed with an acid would be very similar to an Odén sulphur sol, where a layer of the strongly hydrophilic pentathionic acid is adsorbed on the sulphur particles; in their original state the latter would better be called hydrophobic.

The experiments of this paper do not permit final conclusions as to the mechanism of rheopexy. The following are perhaps probable: the special kind of movement used brings the fairly large, anisometric V_2O_5 particles into a position, where the conditions of interaction are

¹¹ A good way of preparing stable rheoplectic V_2O_5 sols might be to add, from the very start, a solution of the complex compound of V_2O_5 with a suitable acid.

somewhat different than in the thixotropic sol, when it is left to itself. As was mentioned above, it has not been proved that the orientation of the particles parallel to each other, brought about by the gentle movement, is instrumental. It is quite possible that the particles may touch each other more easily and more closely, when moved, and then form strings and a kind of network. One is dealing with the same difficulty as one encounters, when trying to explain thixotropy.¹² In any event, in both cases a large amount of liquid may be interlocked and a solid gel is formed.

If, however, the particles are not coated with a hydrated layer, the repelling forces are not sufficiently strong to keep them apart: the movement used may favour a mechanical coagulation,¹³ not a rheoplectic gel formation. This is what probably happens with salts such as KCl, etc., whereas with Li salts and acids the hydrated layer prevents true coagulation and allows a rheoplectic behaviour. Thus rheopexy appears to be, to a certain extent, an intermediate state between a stable sol and a coagulation caused by stirring; just as thixotropy may represent an intermediate state between a stable sol and a coagulation caused by electrolytes. There actually seems to exist a fairly close relation between rheopexy and mechanical coagulation.

The influence of hydrated layers upon rheopexy seems to show that one is not dealing with primary attracting forces between the particles, even if it should turn out that a close touch between the particles is the decisive factor, not orientation.

One influence, so far unmentioned, must be referred to, *viz.*, that of the ζ -potential of the particles. In thixotropy it has to have an intermediate value between the high value in stable sols and the low one, when coagulation occurs. Rheopexy seems to be bound to an even narrower range of suitable ζ -potentials.

Summary.

1. Rheopexy, *i.e.*, the solidification of thixotropic sols by gentle and regular movement was investigated in V_2O_5 sols containing electrolytes. Freshly prepared V_2O_5 sols with amicromic particles were only thixotropic, not rheoplectic. But as soon as large, needle-shaped V_2O_5 particles had been formed in the course of a long time or by careful treatment at higher temperature, the sols became rheoplectic.

2. Not all electrolytes are suitable for producing rheopexy in these sols: rheoplectic sols may be made with Li salts and acids, not with K and NH_4 salts, though the latter can produce thixotropic V_2O_5 sols. The special activity of Li salts and acids is probably due to the marked hydration of the Li^+ ion, and to the fact that the acids can form strongly hydrated complex compounds on the surface of the particles.

3. Li salts and acids are weak coagulants for V_2O_5 sols. This is an anomalous behaviour so far as acids are concerned, since negative sols are generally coagulated more strongly by H^+ ion than by the other inorganic, monovalent cations. V_2O_5 sol resembles in this respect Odén's sulphur sol.

4. Rheopexy is closely related to coagulation by stirring; it may be considered to be an intermediate state between a stable sol and one coagulated by stirring, just as thixotropy may in many cases be assumed

¹² Cf. for instance, Freundlich, *Thixotropy*, Paris, 1935, pp. 10-11.

¹³ Cf. Freundlich and Kroch, *Z. physik. Chem.*, 1920, 124, 155; Freundlich and Loebmann, *ibid.*, 1928, 139, 368; *Kolloidchem. Beiheft*, 1929, 28, 391.

to be an intermediate state between a stable sol and one coagulated by electrolytes.

We desire to express our sincere gratitude to Professor H. Freundlich whose steady advice and many suggestions during the work were a great help to us. We also would like to thank Mr. C. F. Goodeve, M.Sc., for valuable discussions. Our hearty thanks are due to Professor F. G. Donnan, F.R.S., for his hospitality.

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THE OXIDATION OF CARBON.

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It is well known that oxygen can undergo chemisorption on the surface of carbon to give some form of surface oxide layer. Schilow¹ and Kolthoff² have demonstrated the existence of different specific oxide complexes on the carbon surface, which are formed under definite conditions and show acidic or basic properties. Such surface oxides will clearly play some part in the oxidation process of carbon.

In order to investigate the kinetics of the primary oxidation process it is necessary to eliminate the effect of the rate of diffusion of gas to and from the surface. This may be done either by working with a small filament at temperatures of 800° to 1200° C. and at very low pressure, or with a large surface (granules) at normal pressures and at relatively low temperatures where the very slow surface reaction is the controlling factor. The experimental results which have been obtained by both methods are very varied, but may be divided into two main groups: on the one hand Langmuir³ working with filaments at 950° C. found a formation of pure carbon dioxide by impact of oxygen molecules on the *clean* carbon surface—the process being *retarded* by formation of oxide layer: on the other hand Langmuir, working at higher temperatures, Sihvonen,⁴ Eucken,⁵ and Meyer,^{6,7} working with filaments over a wide temperature range, and Rhead and Wheeler,⁸ working with charcoal granules at temperatures in the neighbourhood of 500° C. found primary formation of *both* carbon dioxide and carbon monoxide by various different mechanisms involving the breakdown of surface oxide complexes. The

¹ Schilow, *Z. physik. Chem.*, 1930, 149, 211.

² Kolthoff, *J.A.C.S.*, 1932, 54, 4473.

³ Langmuir, *J.A.C.S.*, 1915, 37, 1154.

⁴ Sihvonen, *Z. Elektrochem.*, 1934, 40, 456, and many earlier papers in *Annal. Acad. Scient. Fenn.*

⁵ Eucken, *Z. angew. Chem.*, 1930, 43, 986.

⁶ Meyer, *Z. physik. Chem.*, 1932, 17B, 385.

⁷ Martin and Meyer, *Z. Elektrochem.*, 1935, 41, 141.

⁸ Rhead and Wheeler, *J.C.S.*, 1912, 101, 846.

wide divergence between the results of different experimenters must be due either to difference in experimental conditions, or to difference in the nature of the carbon surface used. We have attempted to correlate different types of mechanism by investigating the oxidation of several different kinds of carbon under standard experimental conditions.

Experimental Method.

The experimental method was to pass mixtures of oxygen and nitrogen at steady and accurately measured rates over a granular carbon packed in a silica tube, which was heated in an electric furnace, and to collect and analyse a sample of the gas coming off when a steady state was reached. The length of time for which the gas is in contact with the carbon was inversely proportional to the rate of flow and by measuring the percentage reaction at different flow-rates it was possible to obtain a curve showing the course of the reaction with time. The experiments were all conducted at atmospheric pressure, but the initial oxygen concentration could be varied by altering the proportions of oxygen and nitrogen in the mixture.

The apparatus is shown in Fig. 1(a). Oxygen and nitrogen were obtained from cylinders fitted with reducing valves and the flow-rates could be accurately adjusted and measured by adjustable blow-off bubblers "A" and venturi flow-meters "B."

The cylinder gases used were analysed from time to time and were always found to be at least 99.5 per cent. pure. The percentage compositions of mixtures of oxygen and nitrogen calculated from flow-meter readings agreed with those obtained by check analyses within 0.5

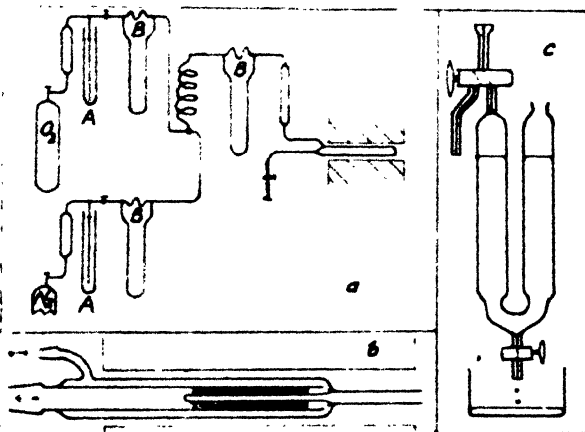


FIG. 1.

per cent. The carbon was contained in a silica tube, Fig. 1(b) specially designed to ensure a steady flow of preheated gas through the granules. The temperature was measured by a thermocouple inside the carbon bed and controlled to within $\pm 1^\circ \text{C}$. by hand adjustment or (in the later stages of the work) by a Cooke and Swallow automatic regulator. The reaction was not sufficiently rapid for the temperature to be affected by the heat developed in the combustion. Gas samples of 20 c.c. were collected over mercury in a collector shown in Fig. 1(c) which allowed the sample to be taken at constant pressure without appreciably disturbing the flow-rate. The gas analyses were made in an apparatus designed by B. Lambert (description not yet published). Approximately 20 c.c. of carbon granules were used in each set of experiments and the gas was passed at flow-rates varying between 2 c.c. per minute and 10 c.c. per minute. The attainment of a "steady state" after the setting of temperature and flow-rate was checked by taking samples at intervals of half an hour and analysing for carbon dioxide—agreement between the percentages of CO_2 obtained by analysis of

two successive samples to within 0.5 per cent. being regarded as a sufficient criterion. The "steady state" was usually reached after about two hours: the accuracy of the experimental results was ensured either by analysing two successive samples as above, or by allowing at least three hours between setting and sampling. It was thus possible to obtain three or four readings in one day's "run." The error due to burning away of the carbon surface during this time was checked for each type of carbon by occasionally repeating the initial reading at the end of the day; the percentage reaction usually showed a steady decrease of 2 per cent. or less. A complete series of readings to demonstrate some particular point—course of reaction, oxygen concentration effect, or temperature coefficient—was always taken on a single day so as to eliminate as far as possible errors due to alteration in the carbon surface.

Experimental Results.

Four kinds of carbon were used: steam-activated coconut charcoal granules, steam-activated anthracite granules, granules of pure graphite, and diamond dust. The coconut charcoal

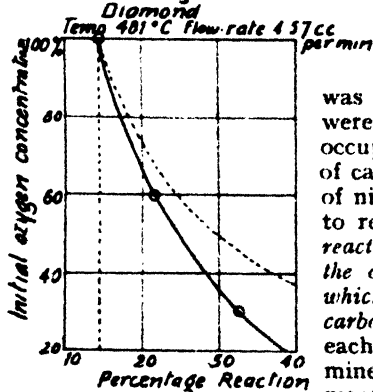
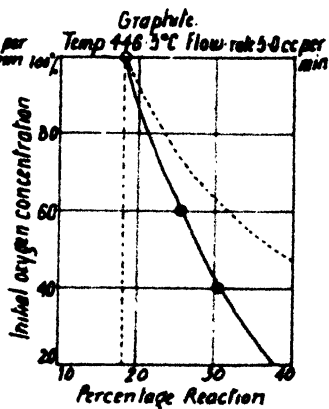
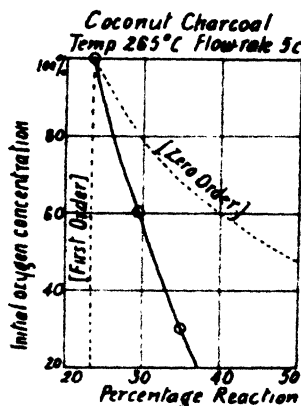


FIG. 2.—Effect of Initial Oxygen Concentration.

was obtained commercially and ten grams were spread on clean asbestos wool so as to occupy a convenient volume. Each sample of carbon was heated to 1000° C. in a current of nitrogen for several hours before use so as to remove moisture. The term "percentage reaction" is used to indicate the percentage of the oxygen present in the initial gas mixture which has been converted to carbon dioxide or carbon monoxide. The temperature range of each set of experiments is arbitrarily determined by the relation between the rate of reaction and the available rates of flow.

The Course of Reaction is shown by Table I. and approximates closely to first order.

The Effect of Initial Oxygen Concentration is shown in Fig. 2. For a true first order reaction the percentage reaction in a given time is independent of the initial oxygen concentration. This is clearly not so in the

and diamond dust. The coconut charcoal and anthracite were clean, hard granules and so graded that different samples gave results which were almost quantitatively identical. The graphite granules were cut by hand from a lump of pure natural Ceylon graphite. The diamond dust

was obtained commercially and ten grams were spread on clean asbestos wool so as to occupy a convenient volume. Each sample of carbon was heated to 1000° C. in a current of nitrogen for several hours before use so as to remove moisture. The term "percentage reaction" is used to indicate the percentage of the oxygen present in the initial gas mixture which has been converted to carbon dioxide or carbon monoxide. The temperature range of each set of experiments is arbitrarily determined by the relation between the rate of reaction and the available rates of flow.

Coconut Charcoal burnt in the neighbourhood of 250° C. giving carbon dioxide

TABLE I.—COURSE OF REACTION WITH TIME.

Type of Carbon, etc.	Flow Rate = $\frac{1}{2}$ l.	Percentage Reaction.	First Order Reaction Const.
	c.c./min.		
Coconut Charcoal	8.93	23.5	2.39
Temp. 267° C.	6.06	33.0	2.43
Initial O ₂ concn. 43.8 per cent.	3.37	51.4	2.43
Graphite	8.93	17.0	1.66
Temp. 446° C.	3.33	41.2	1.77
Initial O ₂ concn. 44.1 per cent.	2.0	58.3	1.75
Diamond	8.06	17.0	1.50
Temp. 481° C.	3.33	37.8	1.58
Initial O ₂ concn. 40 per cent.	2.0	53.5	1.49

TABLE II.—RETARDATION BY CARBON DIOXIDE.

Type of Carbon, etc.	Initial O ₂ Percentage.	Initial N ₂ Percentage.	Initial CO ₂ Percentage.	Percentage Reaction.
Coconut Charcoal	40	0	60	28.2
Temp. 277° C.	40	60	0	35.0
Flow-rate, 6.0 c.c. per min.	80	20	0	24.0
Graphite	50	0	50	{ 25.8
Temp. 450° C.	50	50	0	{ 28.0
Flow-rate 5.0 c.c. per min.				{ 32.0
Diamond	100	0	0	8.3
Temp. 474° C.	50	0	50	{ 7.8
Flow-rate 4.8 c.c. per min.	50	50	0	{ 9.2
				{ 11.0
				21.4

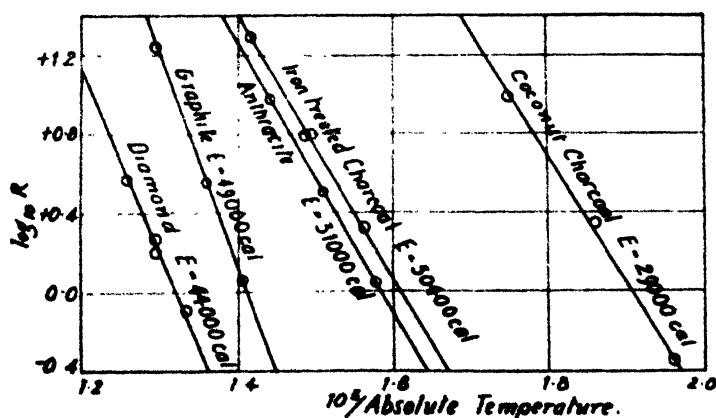


FIG. 3.—Effect of Temperature.

present case and the deviations are such as would be accounted for by supposing either that the reaction is of less than first order with respect to oxygen—or that it is retarded by carbon dioxide.

The effect of carbon dioxide was investigated by comparing the percentage reaction given by oxygen diluted by nitrogen with that given by oxygen diluted by the same percentage of carbon dioxide under identical conditions. The results of a series designed to show both the retardation by carbon dioxide and the effect of initial oxygen concentration (see discussion later) are shown in Table II. It was very difficult to obtain steady values with carbon dioxide as diluent and the results are not quantitatively reproducible, but there is clearly a small retardation by carbon dioxide.

The Effect of Temperature is shown in Fig. 3. Values of the reaction constant " k " were calculated on the assumption that the reaction follows a first order course and $\log k$ was plotted against the reciprocal of the absolute temperature. The points fell closely on a straight line of slope corresponding to an Energy of Activation of 29,000 Cal. The close agreement with Arrhenius' Law and the high value of E indicate that the experimental results are real measurements of a true chemical reaction and are not influenced by accidents of flow and diffusion.

Graphite and Diamond both burn to pure carbon dioxide in the neighbourhood of 400° C. and 500° C. respectively. The kinetics are similar to those obtained with coconut charcoal. The experimental results are shown in Figs 2 and 3 and Tables I. and II.

Discussion of the Kinetics of the Oxidation of Coconut Charcoal, Graphite and Diamond.

These three reactions are very similar and all show the same apparent discrepancy between an accurately first order course of reaction and an effect of initial oxygen concentration which tends strongly to zero order. It is possible to develop a quantitative theory which will account for this on the basis of Langmuir's idea³ of a direct formation of carbon dioxide, the reaction being retarded by the simultaneous formation of a stable surface oxide layer. We must assume *in addition* that a similar retarding layer is *also* formed by carbon dioxide. If it be further assumed that carbon dioxide *formed in the reaction* is retained by the surface and held approximately as firmly as the oxygen in the retarding film we may obtain for the rate of reaction

$$\frac{d[\text{CO}_2]}{dt} = \frac{k[\text{O}_2]}{1 + b\{[\text{O}_2] + [\text{CO}_2]\}} \quad (1)$$

Since $\text{O}_2 + \text{C} \rightarrow \text{CO}_2$ the factor $\{[\text{O}_2] + [\text{CO}_2]\}$ is equal to the initial oxygen concentration and constant throughout the course of the reaction, which will obey a first order expression :

$$\frac{d[\text{CO}_2]}{dt} = \frac{k[\text{O}_2]}{1 + \text{const.}} = k'[\text{O}_2].$$

When the initial oxygen concentration is varied, if " a " be the initial oxygen concentration and " x " the amount which has reacted at time " t ," we may write

$$\frac{dx}{dt} = \frac{k(a - x)}{1 + ba}.$$

This integrates to give

$$k = \frac{1 + ba}{t} \ln \frac{a}{a - x}.$$

This contains two unknown constants " k " and " b " and may be tested by solving for " b " and " k " from two experimental settings and using these values to calculate for a third oxygen concentration a theoretical value of " x " which may be compared with the experimental result. The agreement obtained is satisfactory as shown in Table III.

TABLE III.—THE EXPERIMENTAL VALUES TAKEN ARE THOSE SHOWN IN FIG. 2.

Type of Carbon.	Values used to Calculate " b " and " k ."		" b ."	" k ."	Initial O ₂ Concentration to be Tested.	Percentage Reaction.	
						Calculated.	Observed.
Coconut Charcoal .	40	30.7	0.027	3.84	60	25.3	25.8
	100	18.6					
Graphite . . .	100	14.5	0.064	5.28	60	21.4	21.8
	30	32.8					
Diamond . . .	100	23.5	0.012	3.01	60	29.1	29.5
	30	35.5					

The assumption that carbon dioxide *formed in the reaction* is adsorbed with about the same firmness as oxygen would hardly be expected to apply to carbon dioxide added externally. The experimentally observed retardation by carbon dioxide (Table II.) is indefinite and much less than that demanded by equation (i), which would predict the percentage reaction for any mixture of oxygen and carbon dioxide to be the same as that for pure oxygen. In the case of diamond, which being more homogeneous might be expected to show simpler adsorption characteristics than charcoal or graphite, there is some approximation to the theoretically predicted retardation.

Molecular Statistics of the Reaction.

The actual rate of a heterogeneous gas reaction at a given temperature is determined by the number of gas molecules striking the surface in unit time and by the activation energy. It may be shown from the kinetic theory that :

$$\frac{1}{3} \frac{v \lambda}{A} = e^{-E/RT} \quad (2)$$

Where " x " is the fraction of molecules which react when a gas streams at velocity v cm./sec. over a surface of area A sq. cm. This equation cannot be applied quantitatively to our results in default of any accurate knowledge of the surface areas used, but a *qualitative* test of the validity of the energies of activation obtained may be made by calculating A from the observed values of E and x and observing whether the results are plausible. An abnormally large value of A will indicate that the reaction takes place much faster than would be expected from its energy of activation—and vice versa. The results of the calculation are shown in Table IV.

It is clear that for graphite and diamond the calculated values of A are absurdly high, showing that the reaction takes place much faster than its energy of activation should permit. It is inconceivable that

TABLE IV.

Type of Carbon.	<i>E</i> .	<i>A</i> (Calculated).	<i>A</i> (Measured in Other Ways).
Coconut Charcoal .	29,000 Cal.	$1.6 \times 10^8 \text{ cm.}^2$	Rough values given in the literature—calculated from adsorption data. $1.8 \times 10^8 \text{ cm.}^2$ $1.46 \times 10^7 \text{ cm.}^2$
Anthracite . . .	31,000 Cal.	$5.4 \times 10^4 \text{ cm.}^2$	Adsorptive capacity for vapours $\frac{1}{3}$ that of coconut charcoal.
Graphite . . .	49,000 Cal.	$9.15 \times 10^8 \text{ cm.}^2$	External surface of granules estimated from average granular size. $2.7 \times 10^2 \text{ cm.}^2$
Diamond . . .	44,000 Cal.	$9.0 \times 10^8 \text{ cm.}^2$	

the surface area of graphite granules, or even of diamond powder should be larger than that of highly active charcoal and the effect can only be explained if it be supposed that *E* is *not* the true energy of activation in these two cases, but contains other terms which give the reaction an abnormally high temperature coefficient. There are two possibilities :

(i) A retarding layer begins to evaporate off the surface at higher temperatures but is stable at the lower temperatures of the coconut charcoal oxidation. (It is interesting to note that the "Oxide C" described by Schilow *begins* to be thermally unstable at temperatures above 400° C.).

(ii) The available surface increases at higher temperatures owing to the opening up of cracks.

Calculation of an energy of activation for the graphite oxidation by equation (2) from the measured surface area of the graphite granules, which is probably of the right order, gives a value of 27,000 Cal. (*cf.* *E* = 29,000 Cal. for coconut charcoal). This suggests that the two oxidation processes are essentially the same in both kinetics and energy but that the temperature coefficient for the oxidation of graphite is modified by the type of effect described.

Experimental Results with Anthracite.

The anthracite granules burnt at about 400° C. to give a mixture of carbon dioxide and carbon monoxide. In the tables below "percentage reaction to carbon monoxide" is the percentage of *oxygen* converted to carbon monoxide, which is equal to *half* the carbon monoxide formed, since $\text{O}_2 + \text{C} \rightarrow 2\text{CO}$ (a correction is applied for the volume increase).

The Course of Reaction is shown in Fig. 4.

The *total* reaction gives a first order curve, but the proportion of carbon dioxide to carbon monoxide increases rapidly with time.

The Effect of Initial Oxygen Concentration is shown in Fig. 5. This shows a very close approximation to the theoretical behaviour of a first order reaction and the $\text{CO}_2 : \text{CO}$ ratio is independent of the initial oxygen concentration.

The Effect of Temperature is shown in Fig. 3. Values of *k* were calculated for the total percentage reaction, assuming a first order course, and log *k* plotted against the reciprocal of θ_{Ab} gave a very straight line corresponding to *E* = 31,000 Cal.

In order to test whether carbon monoxide is a *primary product* a mixture of carbon dioxide and nitrogen was passed over the anthracite at 385° C. No trace of carbon monoxide could be detected in the product.

This is to be expected since even at 500° C. $k = \frac{[\text{CO}]^2}{[\text{CO}_2]}$ for the reaction

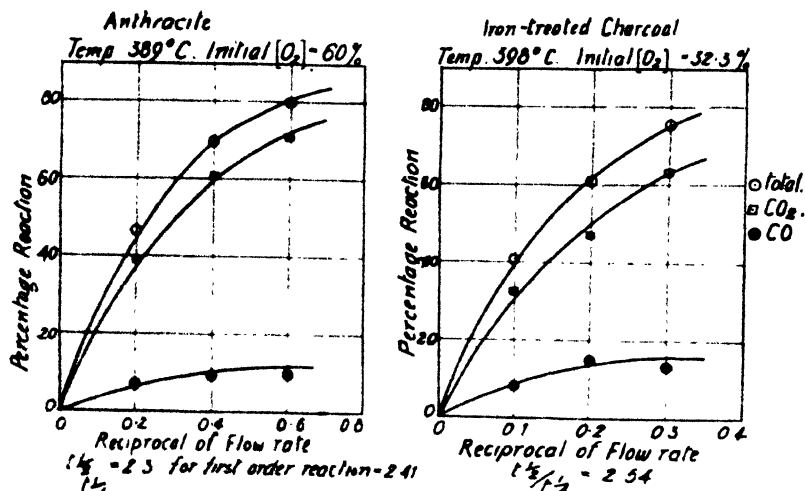


FIG. 4.—Course of Reaction with Time.

$\text{CO}_2 + \text{C} \rightarrow 2\text{CO}$ is $10^{-10.5}$. It would appear that the primary process is a reaction of first order with respect to oxygen giving a mixture of carbon dioxide and carbon monoxide, or possibly pure carbon monoxide; and that the increase in the ratio $\text{CO}_2 : \text{CO}$ with time is due to the reaction

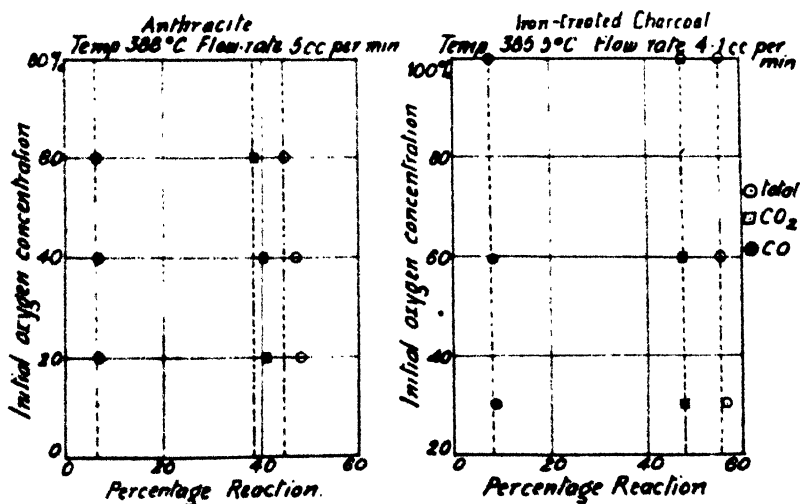


FIG. 5.—Effect of Initial Oxygen Concentration.

$2\text{CO} \rightarrow \text{C} + \text{CO}_2$ which is thermodynamically favoured at this temperature and which has been shown by Rhead and Wheeler to occur fairly rapidly under these conditions. (The effect cannot be due to further oxidation

of CO to CO_2 , as this would mask the simple first order course of the total reaction—and furthermore as the CO_2 :CO ratio is independent of the initial oxygen concentration—see Figs. 4 and 5.)

Experiments on Artificially Treated Charcoals.

It has been shown that graphite and diamond, the purest forms of carbon used, give pure carbon dioxide on oxidation at temperatures of 440° to 480° C.; while anthracite, which is certainly impure, gives a mixture of carbon dioxide and carbon monoxide at 300° C. This suggests that the primary production of carbon monoxide may be due to the presence of some special form of impurity on the carbon surface. Coconut charcoal, which is oxidised at 250° C. to give carbon dioxide with a trace of carbon monoxide and shows the same kinetics as graphite and diamond can be regarded as containing only a trace of this impurity. It is noteworthy that the anthracite, whose energy of activation (31,000 Cal.) is only slightly higher than that of coconut charcoal (29,000 Cal.); and which probably has a similar surface area, oxidises under experimental conditions at a very much higher temperature. It would appear from this that only a portion of the surface is effective. Furthermore while the kinetics of the oxidation of coconut charcoal, graphite and diamond involve a very marked retardation by increased oxygen concentration (Fig. 2), this is almost absent in the anthracite (Fig. 5). We can account for this by supposing that in anthracite the simple, direct formation of carbon dioxide found in the other three cases is practically suppressed by the blocking of those portions of the surface where this is possible. Instead there is a slower reaction in which both carbon dioxide and carbon monoxide are produced by a different mechanism which probably involves the breakdown of a surface oxide complex. This latter process would appear to be *catalysed* in the anthracite and not merely occasioned by the raising of the reaction temperature, as coconut charcoal still gives only a trace of carbon monoxide when oxidised at 400° C. The anthracite therefore differs from the other forms of carbon in that those portions of the surface where direct formation of pure carbon dioxide can take place are blocked, whilst the primary formation of carbon monoxide and carbon dioxide by a different type of process is catalysed.

Attempts were made to treat the coconut charcoal with a substance which would exert this combined *poisoning* and *promoting* effect to give an artificial product reproducing the behaviour of anthracite. The presence of moisture, which has been supposed by some workers to have a profound effect on the interaction of carbon and oxygen, merely retarded the formation of carbon dioxide (presumably by blocking a portion of the carbon surface) without altering either the energy of activation of the reaction or the proportion of carbon monoxide formed. Sodium and Potassium Carbonates (although well known for their influence on the burning of charcoals in general) were similarly ineffective under these conditions. The anthracite was known to contain *iron*, and it was found that after treating a sample of coconut charcoal (which normally burnt at 250° C. under experimental conditions to give carbon dioxide with a trace of carbon monoxide) by "cleaning out" at 1000° C. in a nitrogen stream, boiling in ferric chloride solution, and heating in nitrogen again to remove water, hydrochloric acid, and excess ferric chloride, oxidation at a rate comparable with the original took place only at 400° C., to give a mixture of carbon dioxide and carbon monoxide. The kinetics were investigated and found to be very similar to the kinetics for the oxidation of anthracite.

The Course of Reaction is shown by Fig. 4. The rate falls off with time slightly more rapidly than for a first order reaction. The ratio of carbon dioxide to carbon monoxide increases with time as in the case of anthracite.

The Effect of Initial Oxygen Concentration is shown in Fig. 5 and corresponds accurately to a first order reaction—as with anthracite.

The Effect of Temperature is shown in Fig. 3 $\log k$ plotted against the reciprocal of the absolute temperature gives a straight line corresponding to $E = 30,400$ Cal. (cf. E for anthracite 31,000 Cal.).

The behaviour of two different iron-treated samples of coconut charcoal was very carefully investigated and both showed the same close resemblance to anthracite. The effect only occurs when a charcoal sample *which has been "cleaned" by heating to 1000° C. in nitrogen* is treated with ferric chloride solution. If an uncleaned sample is so treated the oxidation is considerably retarded (the sample burnt under experimental conditions at 350° C.) but no appreciable amount of carbon monoxide is formed. It would appear that the "promotion" depends on intimate adsorption of iron on the most active points of the charcoal surface.

Discussion.

General consideration of the literature shows that two distinct types of process are possible in the oxidation of carbon (see introduction to this paper).

(1) Direct formation of carbon dioxide by impact of oxygen molecules on the *clean* carbon surface, a process which is retarded by the presence of surface oxide layer.

(2) The primary formation of both carbon dioxide and carbon monoxide by mechanisms involving the breakdown of surface oxide layer either spontaneously, or by impact of oxygen molecules from the gas.

Under our experimental conditions pure carbon (whether graphite or diamond) shows exclusively process (1). Process (2) only occurs in the presence of iron (other catalysts may of course have a similar effect) which also poisons the surface for process (1). The action of the catalyst is possibly to decrease the stability of the surface oxide so that it breaks down under the impact of oxygen molecules from the gas to give a mixture of carbon dioxide and carbon monoxide at a rate proportional to the oxygen concentration. A similar decrease in stability may well occur at higher temperatures without the presence of a catalyst. If this is so, process (2) will operate on *pure* carbon at higher temperatures as was demonstrated by Langmuir² who found that on a pure carbon filament at 950° C. process (1) occurs exclusively whilst at temperatures above 1430° C. process (2) begins to operate. We cannot at the present stage in our investigations suggest a detailed mechanism for process (2) in default of information as to the proportions in which carbon dioxide and carbon monoxide are primarily formed. In view of the diversity of surface oxides which can exist¹ it may be that several different mechanisms are possible under varying conditions.

Summary.

Two distinct types of process appear to be possible in the oxidation of carbon:

- (1) Direct formation of carbon dioxide by impact of oxygen molecules on a clean carbon surface.
- (2) Primary formation of both carbon dioxide and carbon monoxide by the breakdown of surface oxide complexes.

The kinetics of the oxidation of several kinds of carbon have been investigated in the temperature range 250°–500° C. by a dynamic method, with a view to correlating the different mechanisms. Pure graphite and diamond showed exclusively process (1). An activated coconut charcoal showed process (1) with a trace of process (2). Activated anthracite,

containing a considerable amount of iron showed exclusively process (2). Treatment of the coconut charcoal with ferric chloride under suitable conditions gave an artificial product whose behaviour on oxidation reproduced very closely that of the anthracite. These results are discussed in relation to the work of other authors.

The author is very grateful to Mr. C. N. Hinshelwood for his interest in the whole work; to Dr. B. Lambert for advice on the experimental technique and for the loan of apparatus; and to Mr. J. H. Strawson who performed some of the experiments.

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STUDIES ON SOL-GEL TRANSFORMATIONS. II. DILATOMETRIC INVESTIGATIONS ON IRON HYDROXIDE, GELATIN, METHYL CELLULOSE, SILICIC ACID AND VISCOSE.

BY ERICH HEYMANN.

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I. Introduction.

It is still a matter of speculation as to the nature of the changes that occur in a colloidal system, when it is transformed from a sol into a gel (jelly), especially whether any changes in hydration of the colloidal particles occur during such a process. Some time ago a paper was published,¹ in which the "inverse" sol-gel transformation of methyl cellulose solutions, forming a reversible gel on heating, was dealt with. The change of the investigated physical (viscosity, density) and chemical (lyotropic series of ions) properties indicated that the gel formation was accompanied by a reversible decrease in hydration of the particles: the viscosity, for instance, measured at constant temperature, at first decreased reversibly and showed the usual increase due to gelation only after a time. This initial reversible viscosity decrease can be explained by a decrease in hydration, since no decrease in particle size takes place during this sol-gel transformation. The volume, investigated in a sensitive dilatometer at constant temperature, increased during the sol-gel transformation. Since we have to assume that hydration water, bound by van der Waals' forces to the particles, has a higher density than free water, this also suggests that the particles become less hydrated during the formation of a methyl cellulose gel.

A comparison of sol-gel transformations of various types of systems in respect to the volume change shows that all possible types can be realised experimentally: systems with no volume change (iron hydroxide), systems which show a decrease in volume (agar, gelatin), and systems which show an increase in volume (methyl cellulose, silicic acid).

¹ E. Heymann, *Trans. Faraday Soc.*, 1935, **31**, 846.

An attempt is made to derive from these experimental facts some information about the structural changes which occur during the various sol-gel transformations.

The total volume contraction, which occurs when a hydrophilic colloid is dissolved in a liquid with the formation of a sol or a gel has been determined many times, *e.g.*, by H. Quincke,² (egg albumin), H. Rodewald³ (starch), C. Davis and E. Oakes,⁴ H. Chick and C. H. Martin⁵ (proteins), J. R. Katz⁶ (casein, nuclein, starch), A. Taffel⁷ (gelatin), The Svedberg⁸ (gelatin), W. J. Mardles⁹ (organosols), and H. A. Neville and E. R. Theis¹⁰ (gelatin). The very small volume changes, however, which occur when a sol is transformed into a gel, have only been measured by W. J. Mardles (acetyl cellulose), by K. Krishnamurti¹¹ (agar), and by the author.¹

The volume change measurements of sol-gel transformations require a much more sensitive dilatometric technique than the determination of the total volume change during the dissolution of a colloid. A sensitive mercury dilatometer for this purpose is described in the next paragraph. The systems for investigations must show a hysteresis, which allows observations on the transformation to be made over a period of hours or days, in order that the time taken for the dilatometer to acquire the temperature of the thermostat can be neglected.

II. Volume Changes during Sol-gel Transformations.

(a) Experimental.

A sensitive dilatometer has already been described.¹ Its main advantage consists in the fact that the sol is only in part I., whereas the whole of part II., including the capillary (b) is filled with mercury (Fig. 1). Vacuum grease was used for coating the tap (c) and the key pressed in by a taut rubber band. This method proved to be very satisfactory. With practice leakage through the tap never occurred. The measurements were carried out in an electrically heated water-thermostat, the temperature of which had a maximum variation of 0.003 to 0.004° . The volume of the sol was about 80 c.c., the radius of the capillary 0.23 mm.; thus a length of 1 cm. in the capillary corresponded to a volume change of 0.0016 c.c. Consequently the smallest volume change, which could be detected with certainty (corresponding to a change of meniscus of 0.1 cm.) was 0.0002 %. As the volume changes usually measured in the investigated systems were between 0.002 and 0.01 % of the total volume (corresponding to a change of height of meniscus from 0.6 to 7.5 cm.) the accuracy of a

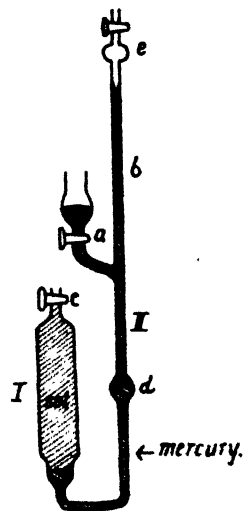


FIG. 1.

¹ H. Quincke, *Pflüger's Archiv.*, 1870, 3, 332.

² H. Rodewald, *Z. physik. Chem.*, 1897, 24, 193.

³ C. Davis and E. Oakes, *J. Amer. Chem. Soc.*, 1922, 44, 464.

⁴ H. Chick and C. H. Martin, *J. biol. Chem.*, 1923, 7, 34.

⁵ J. R. Katz, *Koll. Beih.*, 1917, 9, 20.

⁶ A. Taffel, *Trans. Chem. Soc.*, 1922, 121, 1971.

⁷ Th. Svedberg, *J. Amer. Chem. Soc.*, 1924, 46, 2672.

⁸ W. J. Mardles, *Trans. Faraday Soc.*, 1923, 18, 365; *Kolloid Z.*, 1929, 49, 4.

⁹ H. A. Neville and E. R. Theis, *Coll. Symp. Monogr.*, 1930, 7, 41.

¹⁰ K. Krishnamurti, *Current Science*, 1934, 2, 35.

determination of change in volume was about 1.5 to 12 %, according to the magnitude of the volume change measured.

In many systems, however, the changes in volume are larger than 0.01 %. In these cases ordinary dilatometers without mercury were used. The dimensions varied according to the magnitude of the effect. The capillaries had radii between 0.16 and 0.35 mm., whereas the volume was usually between 30 and 70 c.c. In all these cases, however, a layer of paraffin oil was put above the sol and in the capillary, since it was necessary to prevent the solidifying sol entering the capillary. The ordinary dilatometers were used for investigating the sol-gel transformations of silicic acid and the maturing of viscose, whereas the sensitive mercury dilatometer was used for methyl cellulose, gelatin and iron hydroxide.

In all experiments it was ensured that the temperature equilibrium between the dilatometer and the thermostat had been reached before the first reading was taken. Moreover, precautions were taken to avoid the formation of air bubbles.

(b) Reversible Sol-gel Transformations.

One dilatometric experiment on methyl cellulose (containing 35.4 % methoxyl) has already been described.¹ Thus only the results of the continued experiments will be here described. In series I. the solutions were aged at 35.7°, where the sol is transformed into a very soft gel over a period of two days. In series II. the volume of the sol was measured in the dilatometer at 34.5°, then the dilatometer was transferred into a bath at 55° for half an hour, when the gel was rapidly formed, afterwards the volume of the gel was measured at the same temperature at which the volume of the sol had been measured, namely, 34.5°. The difference in volume between the sol and the gel, obtained in this way was usually larger than in the case of method I.; the reason is that with method II. a stiffer gel is obtained than with method I.

The concentration of methyl cellulose was 1.62 %, the sols containing 0.1 mol. K_2SO_4 in order to lower the transformation temperature for experimental convenience.

It can be seen from the results, given in Table I., that the formation

TABLE I.—VOLUME: 80 c.c.; RADIUS OF THE CAPILLARY: 0.23 mm.

Method.	Difference in Meniscus in cm.	Observed Volume Change.		Volume Change in c.c. Per 100 g. Methyl Cellulose.
		(In c.c.).	(Per Cent).	
I.	0.62	+ 0.00096	+ 0.0012	+ 0.08
	0.61			
	1.05			
	1.00			
II.	0.88	+ 0.0016	+ 0.0020	+ 0.13
	1.00			
	0.98			
	0.98			

of a methyl cellulose gel from the sol is accompanied by a volume increase of 0.08 to 0.13 c.c. per 100 g. solid methyl cellulose.

Several series of experiments were carried out with gelatin solutions and the volume change was measured in relation to the concentration of the gelatin and to

the p_H . Electrodialysed gelatin was used. In this system the volume decreases during the sol-gel transformation. The experiments were carried out as follows. The solution was filled into the dilatometer, then heated to about 50° to be sure that the whole mass was liquid and then placed in the thermostat at a temperature of 22.5°, where the gel formation occurred slowly. The main volume decrease took place within the first few hours; but after the sol had set to a gel the volume decrease

continued for some time. After two days the volume did not change further to any appreciable extent. If the dilatometer with the gel was again heated and replaced in the thermostat the same curve for the volume decrease was obtained. This could be repeated at will.

In Fig. 2 the curves (*a* and *b*) of two experiments show that the reproducibility of the results is fairly good. Curve *c* was obtained, after the dilatometer was placed in ice water, when a stiff gel is formed, and then replaced in the thermostat at 22.5°. It shows that the equilibrium volume of the gel, obtained in this way, is only very slightly below the volumes reached when the sol was transformed into a gel at 22.5° in two days; thus no further, appreciable volume change can be expected after this period.

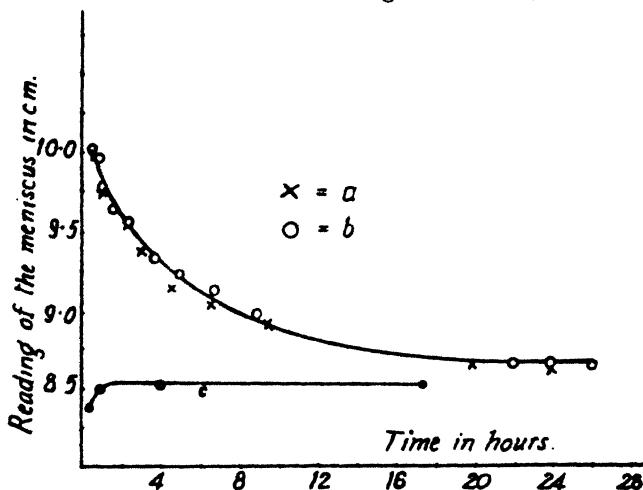


FIG. 2.

Since the first reading has to be taken after the dilatometer has remained in the thermostat for half an hour, the first stages of the transformation cannot be observed and, therefore, the actual volume change may be somewhat larger than the measured one. From Table II. it can be seen that the volume decrease is proportional to the concentration. Furthermore it is independent of the p_H within the limits from 3.8 to 8.8. The volume decrease per 100 g. gelatin is -0.05 to -0.06 c.c.

TABLE II.

Solution.	Difference in Meniscus (in cm.).	Volume of the Solution (in c.c.).	Volume Change.		Volume Change (in c.c. per 100 g. Gelatin).
			(In c.c.).	(Per Cent.)	
1. 4.2 per cent $p_H = 5.5$	1.30	80	-0.0021	-0.0026	-0.052
2. 4.2 per cent. $p_H = 8.8$	1.30	80	-0.0021	-0.0026	-0.052
3. 6.0 per cent. $p_H = 5.5$	1.40	80	-0.0022	-0.0028	-0.068
4. 6.0 per cent. $p_H = 3.8$	1.70	80	-0.0027	-0.0034	-0.057
	1.60	80	-0.0026	-0.0033	-0.056

Many experiments were carried out with several thixotropic iron hydroxide sols. One, with a 0.44 % sol (prepared according to Graham's method), will be referred to, the sol being made thixotropic by adding a small amount of sodium chloride. It can be seen from Table III. that no change of volume occurs during the sol-gel transformation, the meniscus of the dilatometer remaining stationary during the whole experiment.

If we assume that a volume change equivalent to the maximum experimental error occurred, the volume change per 100 g. iron hydroxide would be 0.001 c.c., a value 50 times smaller than that found for gelatin and 100 times smaller than for methyl cellulose. Consequently the volume change (if any) is practically negligible in thixotropic iron hydroxide sols.

TABLE III.

Time in Hours.	Reading of the Meniscus in cm.	Reading of the Beckmann Thermometer.	
0	—	—	liquid
$\frac{1}{2}$	12.50	4.722	"
1	12.50	4.722	"
$1\frac{1}{2}$	12.48	4.720	transition
3	12.50	4.720	soft gel
5	12.50	4.718	"
24	12.52	4.720	gel
47	12.52	4.718	"

(c) Irreversible Sol-gel Transformations.

A very well-known example of an irreversible sol-gel transformation is the formation of silicic acid gels. If solutions

of water glass and hydrochloric acid are mixed in suitable proportions, solutions of silicic acid are obtained which are transformed into gels after several hours. There is much information from other investigations (F. Mylius and E. Groschuff,¹² R. Willstätter, K. Kraut and K. Lobinger¹³) concerning the chemical and physical processes in such systems. At first,

TABLE IV.

Time in Hours.	Readings of the Meniscus (in cm.).	Reading of the Beckmann Thermometer.	Volume Increase (Per Cent).	Volume Increase (c.c. per 100 g. SiO_2).	Remarks.
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(a) 7.6 per cent. SiO_2 and 1.87 N HCl. Volume: 70 c.c.; radius of the capillary: 0.23 mm.; $T = 23^\circ \text{C}$.

$\frac{1}{2}$	17.06	5.220	—	—	liquid
$1\frac{1}{2}$	22.06	5.221	0.012	0.16	"
3	27.10	5.222	0.024	0.34	"
5	29.68	5.220	0.030	0.40	soft gel
24	38.90	5.222	0.052	0.69	clear jelly
78	45.50	5.224	0.069	0.91	—
240	52.8	5.220	0.086	1.14	slightly turbid
720	59.0	5.210	0.102	1.35	syneresis
2040	64.2	5.210	0.113	1.49	—

(b) 6.8 per cent. SiO_2 , 1.78 N HCl. Volume: 38 c.c.; radius of the capillary: 0.33 mm.; $T = 23^\circ \text{C}$.

$\frac{1}{2}$	6.24	5.220	—	—	liquid
1	7.57	5.226	0.012	0.17	"
3	9.36	5.220	0.028	0.41	"
8	11.11	5.223	0.044	0.63	soft gel
24	12.59	5.220	0.057	0.83	clear jelly
92	14.35	5.216	0.073	1.06	slightly turbid
240	15.80	5.212	0.084	1.22	syneresis
816	17.39	5.212	0.100	1.45	—
1536	18.36	5.210	0.109	1.58	—
2500	18.99	5.210	0.115	1.67	—
3200	19.46	5.212	0.120	1.76	—
3800	19.73	5.210	0.122	1.80	—

¹² F. Mylius and E. Groschuff, *Ber.*, 1906, **39**, 116.

¹³ R. Willstätter, K. Kraut and K. Lobinger, *Ber.*, 1925, **58**, 2462; 1928, **61**, 2280; 1928, **62**, 2097.

molecular silicic acid is formed, which is quickly polymerised with the liberation of water ("chemical dehydration") to higher molecular products (polysilicic acids) and finally to colloidal particles. It seemed of interest to investigate such a system by the dilatometric method.

For the experiments water glass solutions, which contained about 12 % SiO_2 were used, the ratio SiO_2 to Na being 1 to 0.85. When such mixtures were observed in the dilatometer, a very quick increase in volume of considerable magnitude was noted within the first few hours. After 3 hours, for instance, the volume had increased by 0.028 %. After this, gel formation began and was complete in about 24 hours, when a clear jelly was obtained, the volume having increased by about 0.06 %. The volume of the so formed gel increased then more slowly; a change of 0.08 % being noted after 10 days and of 0.11 % (*i.e.*, a volume increase of 1.5 c.c. per 100 g. SiO_2) after 3 months. Even after 5 months no final value was reached, the volume increasing still further, but with decreasing velocity. The gels became more and more opalescent and syneresis (about 13 %) was observed. A second mixture showed the same behaviour.

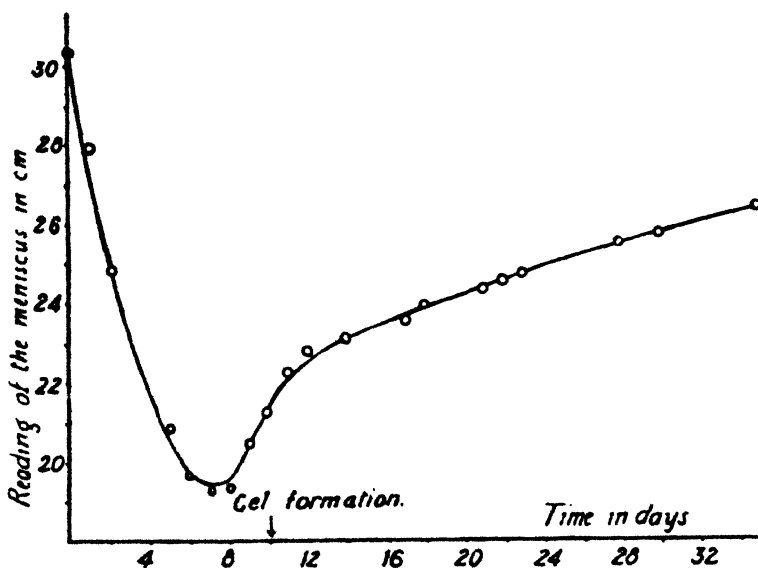


FIG. 3.

(Table IV.) The volume changes in this system are of quite a different order of magnitude compared with those of the previous systems. They are about 10 to 20 times larger.

The last system investigated was a solution of viscose. This system is more complex than the silicic acid gel. It was, however, investigated because of its technical interest.

50 g. cellulose (dense wood pulp)¹⁴ was treated with an 18 % sodium hydroxide solution for about 20 hours. Then the liquid was pressed out until the remaining solid had a weight of about 150 g. This alkali cellulose was aged for 2 days, then 26 g. of carbon disulphide were added and the xanthogenate was formed within 3 hours. The whole mass was now dissolved in 7.2 % sodium hydroxide. The "maturing" of the viscose then commenced. The solution became less viscous at first, then the viscosity increased considerably until a gel was formed, and this finally underwent syneresis.

¹⁴ I am greatly indebted to Dr. Weir (I.C.I. Ltd., Stevenston) for supplying me with a larger quantity of this substance.

This system was measured in the dilatometer. At first the volume decreased rapidly. Then, shortly before the gel formation occurred, the curve changed its direction and the volume increased. This volume increase continued, though slowly. Even after 3 months it did not come to a limiting value. The measured volume changes were of the same order of magnitude as those found with silicic acid solutions (Fig. 3).

III. Volume Change, Hydration and Structural Changes in Reversible Sol-gel Transformations.

There is every likelihood that the volume changes in this group of transformations must be attributed to changes in hydration of the colloidal particles. Since the water bound by secondary forces to the particles has a smaller specific volume than the free water, a volume increase during the transformation accounts for a decrease in hydration. It is very probable that, by measuring volume changes, only that part of the hydration can be distinguished which is caused by an attraction of some kind ("adsorption solvation" by van der Waals and dipole forces; "chemical solvation"), whereas any changes in hydration caused by a mere change in immobilisation of water molecules for purely stereo-metrical reasons cannot be detected in this way.

The justification for these assumptions is given by the fact that hydrophilic colloids allowed to dissolve or to swell in water, cause a considerable decrease in volume of the total system, the water of the hydration layer thus undergoing a process of compression as a result of the attractive forces between the colloidal particles and the water dipoles.

The volume change that occurs during the sol-gel transformation is 50 to 100 times smaller than the volume contraction, which is found when the solid colloid swells or becomes dissolved in the liquid. For instance the swelling of gelatin in water causes a volume decrease of the total system of 5 to 7 c.c. per 100 g. gelatin (Thé Svedberg,⁶ A. Taffel⁷). The volume change during the sol-gel transformation of gelatin, however, is only about 0.06 c.c. per 100 g. gelatin. In the system methyl cellulose-water the volume increase during the sol-gel transformation is 0.13 c.c. per 100 g. solid methyl cellulose. This is about 2 % of the volume contraction that occurs, when methyl cellulose is dissolved in water (7 to 8 c.c. per 100 g. solid methyl cellulose, according to preliminary experiments¹⁵). Thus in both systems the change in hydration during the sol-gel transformation is only a few per cent. of the total hydration.

If we speak in terms of hydration we have, however, to remember that there is no quantitative definition of this term, since the first liquid molecules are bound with a much higher energy than the later ones, and that there is no marked limit to the hydration layer, but a more or less smooth transition to the free water. It is interesting in this connection that the differential heat of swelling decreases gradually with swelling (J. R. Katz⁶).

In the thixotropic iron hydroxide sols no volume change can be detected during the sol-gel transformation, although the technique enables a volume change as small as 0.0002 % of the total volume to be noted. We have, therefore, to assume that there is no change in hydration during the sol-gel transformation of this system. This result is easily understandable. In these thixotropic systems the sol state and the

¹⁵ Not yet published.

gel state are very much alike, both existing at the same temperature, the latter being transformed into the former by comparatively small mechanical forces (H. Freundlich¹⁰).

The "inverse" sol-gel transformation of methyl cellulose, investigated at constant temperature, is accompanied by an increase in volume. Thus the particles become less hydrated whilst the gel is formed. In consequence of this decrease in hydration, large, probably anisometric, coagulates are formed, which build up a loose network, the gel, if the concentration is high enough. H. Staudinger and O. Schweitzer¹⁷ attribute the decrease in hydration to a decomposition of a methyl cellulose-oxonium-hydroxide, which is decomposed, when the temperature is raised. The gel formation of acetyl cellulose in organic liquids is also accompanied by a volume increase (W. T. Mardles⁹).

The opposite behaviour is shown in the sol-gel transformations of gelatin, according to the measurements described in this paper, and of agar, according to the investigations of K. Krishnamurti.¹¹ The transformation, investigated at constant temperature, is accompanied by a decrease in volume and, consequently, it can be assumed that hydration increases. This assumption is in agreement with the experiments of A. Taffel and of Th   Svedberg, who found that the volume contraction, which occurs when gelatin is dissolved in water, is larger at lower temperatures, where a gel is formed, than at higher ones, where sol formation occurs.

When an isoelectric gelatin sol sets to a gel, the gelatin molecules come nearer together and aggregation occurs to a certain degree, as indicated by ultramicroscopic investigations (W. Bachmann¹⁸ and K. Krishnamurti¹⁹) and by measurements of the scattering of light (F. G. Donnan and K. Krishnamurti¹⁹). It seems likely that the equilibrium between the gelatin molecules and the polymolecular aggregates is shifted in the direction of the aggregates, when the gel is formed. The gelatin molecules are arranged in these aggregates (micelles) with a certain regularity, since the X-ray diagrams of the gels show interferences (J. R. Katz, J. C. Derkson and W. F. Bon²⁰). But it is known from Bungenberg de Jong's²¹ and from Katz' investigations, that this aggregation is not accompanied by a dehydration. In fact the volume change measurements show that hydration increases slightly during this process. This has already been suggested by Katz and Derkson. Aggregation and increase in hydration are, however, not related to each other, for, whereas the amount of aggregation is dependent on the p_H , the increase in hydration is independent of the p_H .

Only one fact seems at first to disagree with the assumption of a change in hydration during the sol-gel transformation of gelatin. The dielectric constant, measured by Kistler,²² does not change during this process. However, it appears doubtful whether this method is sufficiently sensitive to detect a small change in hydration. For we have

¹⁰ H. Freundlich, *Kapillarchemie*, vol. II.

¹¹ H. Staudinger and O. Schweitzer, *Ber. Deutsch. Chem. Ges.*, 1930, **63**, 2337.

¹⁸ W. Bachmann, *Z. anorg. Chem.*, 1912, **73**, 125; R. Zsigmondy, *Kolloidchemie*, I., p. 58 (5th edition).

¹⁹ K. Krishnamurti, *Proc. Roy. Soc.*, 1929, **124**, 640; *Nature*, 1929, **124**, 690; F. S. Donnan and K. Krishnamurti, *Colloid Symp. Monogr.*, 1930, **7**, 1.

²⁰ J. R. Katz, J. C. Derkson and W. F. Bon, *Rec. Trav. Chim. Phys. Bas.*, 1931, **50**, 725; 1932, **51**, 514.

²¹ H. Bungenberg de Jong, *Z. phys. Chem.*, 1927, **130**, 205.

²² G. S. Kistler, *J. phys. Chem.*, 1931, **35**, 815.

seen that the hydration change during the sol-gel transformation is only a few per cent. of the total hydration. The effect of the total hydration on the dielectric constant corresponds to the difference between the dielectric constant of water (80) and that of a gelatin solution in a region of wave-length, where the gelatin dipoles do not contribute to the orientation polarisation. This difference is 2 to 3 units for a 0.9 % solution (J. Errera²³). Consequently we have to expect for the sol-gel transformation of a 5 % gelatin solution a decrease in dielectric constant not greater than 0.2 units. This is probably below the limit of accuracy of dielectric constant measurements in systems with conductivity.

One might object that the volume changes observed during the sol-gel transformations of methyl cellulose, agar and gelatin are not necessarily connected with a change in hydration, but that they are the result of an aggregation of the colloidal particles. In this case, however, one would have to assume that the aggregation causes a volume increase in the case of methyl cellulose and a volume decrease in the case of gelatin and agar; a behaviour which would not be easily understandable. There are, moreover, other reasons which make such assumptions very unlikely.

(1) In the case of methyl cellulose a decrease of hydration of the particles during the sol-gel transformation seems likely not only as a result of the volume change measurements. The minimum in the isothermal viscosity curve as well as the influence of the lyotropic series of ions also indicate that a decrease in hydration occurs in this system (E. Heymann). Moreover, a decrease in hydration has to be expected for chemical reasons (Staudinger and Schweitzer).

(2) In the system gelatin-water it has been found by measurements of the scattering of light (Kraemer and Dexter²⁴) and of the sedimentation velocity in the ultracentrifuge (Krishnamurti), that particle aggregation does not occur if the p_H is larger than 7.5 and smaller than 4. Thus if the volume decrease during the gel formation were due to aggregation, it should be dependent on the p_H and it should have a maximum at the isoelectric point. The measurements mentioned in section II. show, however, that the volume decrease is independent of the p_H . To add further point to these arguments, it would, however, be interesting to investigate the X-ray spectra during the gel formation of gelatin (Katz) at various H^+ ion concentrations.

IV. Physical and Chemical Changes during Irreversible Sol-gel Transformations (Silicic Acid, Viscose).

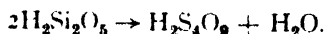
Here the formation of a gel is in many cases the result of a chemical reaction in a solution where a colloidal product is formed. If the volume changes of such transformations are to be investigated, care must be taken to determine the actual process, to which the volume change is due, which may be either the original chemical reaction or the colloidal changes, which the reaction products undergo during the ageing of the system.

If sodium silicate solution is mixed with hydrochloric acid, molecular silicic acid is formed together with sodium chloride. This ionic

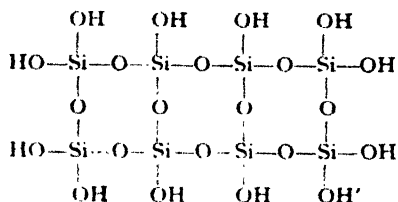
²³ J. Errera, *J. Chimie physique*, 1932, **29**, 577.

²⁴ Kraemer and Dexter, *J. Physic. Chem.*, 1927, **31**, 764.

reaction has a high velocity, so that it has reached completion before measurements in the dilatometer can be made. Every observation after admixture of the original compounds is connected with changes of the silicic acid. We know from the investigations of Willstätter that the originally formed compounds, mono-silicic acid and di-silicic acid undergo polymerisation, for instance



In this way high molecular silicic acids, and in the end colloidal particles, are formed to which we may attribute a configuration of the following kind (E. K. Rideal²⁵):



Every step of this polymerisation is accompanied by a liberation of water molecules. So the very large volume increase observed in the first hours of the reaction until gel formation occurs (0.8 c.c. per 100 g. SiO_2) can be easily understood. It is, however, significant, that after the sol has set to a stiff gel, the volume increase still continues and even 5 months after the gel formation there is no sign of its reaching a limit. The volume increase which occurs after the gel formation is about 1 c.c. per 100 g. silicium dioxide, that is to say, it is more than ten times as large as the whole volume change in the methyl cellulose system. A continuous volume increase of this magnitude has most likely to be explained by the assumption that dehydration reactions are going on in the colloidal particles (R. Schwarz²⁶) and perhaps between the colloidal particles, whereby water molecules are liberated. In this way a network of primary chemical bonds may be established, which may perhaps go through the whole gel; there is, however, no direct experimental proof for this assumption.

A decrease in hydration in regard to water molecules bound by secondary forces may at the same time take place, since more and more hydroxyl groups, the centres of attraction for the water dipoles disappear.

The assumption of a network of primary chemical bonds between the particles in silicic acid gels may explain the high mechanical strength of these gels and the non-existence of thixotropy, as has already been pointed out by Freundlich.²⁷ It explains perhaps, too, why such gels, if dried, do not shrink indefinitely with progressive dehydration, but maintain their volume after a certain stage of drying has been reached.

The processes which take place during the maturing of viscose solutions, leading eventually to the formation of a gel, are much more complicated. It is not the purpose of this paper to discuss these processes

²⁵ E. K. Rideal, *Trans. Faraday Soc.*, 1936, **32**, 3.

²⁶ R. Schwarz, O. Liede and F. Stoenner, *Ber.*, 1920, **53**, 1509; *Koll. Beih.*, 1924, **29**, 171.

²⁷ H. Freundlich, *Thixotropy*, (*Actualités Scientifiques et Industrielles; The Colloidal State*, I.), p. 47, 1935.

in detail and, therefore, only some points are mentioned. The fresh solutions contain most probably a cellulose xanthogenate, which undergoes hydrolysis, whereby NaOH and CS_2 are produced and cellulose is regenerated. Whilst the process of maturing proceeds, the sol becomes more and more hydrophobic (R. O. Herzog and R. Gaebel,²⁸ H. Bungenberg de Jong²¹), the quantities of ammonium chloride required for precipitation becoming gradually smaller. The viscosity, investigated at constant temperature decreases at the beginning and only increases after a time (T. Mukoyama,²⁹ E. Berl and J. Bitter,³⁰ E. Heuser and M. Schuster,³¹ K. Atsuki³²). In this respect this system is similar to the system methyl cellulose-water. Mukoyama has assumed that the minimum in the viscosity curve is due to two processes (1) a decrease in hydration of the cellulose particles, which causes a decrease and (2) the succeeding gel formation which causes an increase in viscosity. It is understandable that a decrease in hydration occurs with increasing hydrolysis, since the cellulose particles are deprived of their hydrophilic xanthogenate groups. The volume curve of the ageing of viscose solution shows a minimum too, as has been shown in Section II. The first decrease is most probably due to the hydrolytic decomposition of the xanthogenate, whereby strongly hydrated ions, such as OH^- and Na^+ are formed. The increase in volume, which is observed later, is most probably the result of the progressive dehydration of the cellulose particles during the gel formation and during syneresis.

Summary.

(1) The volume changes, which occur during the sol-gel transformations of iron hydroxide, gelatin and methyl cellulose have been measured with a sensitive mercury dilatometer; the limit of its accuracy being 0.0002 % of the total volume.

(2) In the case of methyl cellulose the volume increases during the gel formation, in the case of gelatin the volume decreases. The effect is independent of the p_{H} . The magnitude of this volume change is only a few per cent. of the volume changes, which are observed when gelatin or methyl cellulose are dissolved in water. No volume change occurs during the thixotropic sol-gel transformation of iron hydroxide.

(3) A discussion of the possible causes of the volume changes leads to the assumption that a change in hydration of the colloidal particles is responsible for it. Thus the sol-gel transformation of methyl cellulose is accompanied by a decrease, the sol-gel transformation of gelatin by an increase in hydration, whereas in the system iron hydroxide-water no change in hydration occurs. The change in hydration of gelatin and methylcellulose during the gel formation is, however, only a small percentage of the total hydration.

(4) The formation of silicic acid gels from mixtures of sodium silicate and hydrochloric acid was also investigated by means of a dilatometer. The volume increases considerably, its total change being 10 to 20 times larger than in the previously mentioned systems. After the formation of the gel there is a further increase in volume which continues for many months. It is suggested that a chemical dehydration as a consequence of continual polymerisation processes may be the reason for these large

²⁸ R. O. Herzog and R. Gaebel, *Koll. Z.*, 1924, **35**, 193.

²⁹ T. Mukoyama, *Kolloid Z.*, 1927, **41**, 70; **42**, 350; **43**, 349.

³⁰ E. Berl, J. Bitter and E. Lange, *Cellulosechemie*, 1926, **7**, 137, 145.

³¹ E. Heuser and M. Schuster, *Cellulosechemie*, 1926, **7**, 17.

³² K. Atsuki, *J. Fac. Engin., Tokyo, Imp. Univ.*, 1923, **17**, 1935.

volume changes and that these processes progress even after the gel formation.

(5) The maturing of viscose solutions, which involves the formation of a gel that undergoes syneresis, has been investigated dilatometrically and the processes accompanying these changes are briefly discussed.

I am greatly indebted to Professor F. G. Donnan, C.B.E., F.R.S., and to Professor H. Freundlich for their interest and for valuable discussions.

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STUDIES IN CHEMISORPTION ON CHARCOAL. PART VII. THE ADSORPTION OF WATER VAPOUR.

BY C. G. LAWSON.

Received 11th November, 1935.

In a previous publication¹ the effect of activation of charcoal on its adsorption of water vapour in the presence of air was studied. Charcoal activated at low temperatures was found to be far more hygroscopic than that activated at high temperatures. This was correlated with the presence of surface oxides on the charcoal, that which is stable below about 550° C. being acidic² in nature and that stable at higher temperatures being basic and far less hygroscopic. There is no evidence for a sharp transition from one oxide to the other, Rhead and Wheeler³ having shown that the quantity of chemisorbed oxygen varies in a continuous manner with temperature, there being evidence of extra stability between 350° C. and 500° C., which may correspond with the acid surface oxide. A study of the p_H values of charcoal suspensions⁴ shows a gradual change from acidity of charcoal which has been activated at low temperatures to maximum alkalinity at an activation temperature of about 850° C.

On standing in air, a charcoal which had been activated at a high temperature adsorbed more water than before.¹ This is probably due to the reversion of the high-temperature surface oxide to that stable at low temperatures. The p_H values of suspensions show a similar effect.⁴ As a result of this process, the establishment of true adsorption equilibrium is not possible in the presence of air. On plotting curves of the amount of adsorption against time (or better, of the logarithms of these quantities), the process was found to consist of two parts. There was first a rapid increase in the amount adsorbed, then a very slow increase lasting for at least six months. If the charcoal had stood in air for some months before the measurements were started, then this break

¹ A. King and C. G. Lawson, *Trans. Faraday Soc.*, 1934, 30, 1094.

² I. M. Kolthoff, *J. Amer. Chem. Soc.*, 1932, 54, 4473.

³ T. Rhead and R. Wheeler, *J. Chem. Soc.*, 1912, 831 and 846.

⁴ A. King, *J. Chem. Soc.*, 1935, 889.

in the amount of adsorption did not occur. It is therefore due to the building up of surface oxide, rather than to its displacement by water vapour. This effect is particularly marked at low humidities (about 50 per cent. R.H.).

Another drawback to working in the presence of air is the long time required for even approximate equilibrium. This time is some days, or even weeks. It was therefore decided to repeat and extend the earlier work, using a vacuum method. In order to increase the rate of establishment of equilibrium still further, a temperature of 80° C.

was employed, since Coolidge⁵ has shown that equilibrium is not attained readily at low pressures at low temperatures.

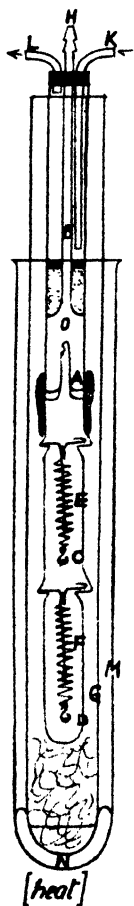


FIG. 1.

Experimental.

The preparation and activation of the sugar charcoal employed was the same as in previous work.¹ Since the charcoal to be studied is covered with surface oxide which is metastable in the absence of air or oxygen, the method used must not involve baking out at high temperatures. The evolution of small amounts of gas (oxides of carbon) from the charcoal during the determination of the adsorption isotherm must therefore be allowed for. The only satisfactory way is to work with a pump sealed on to the apparatus. As the measurements were to be carried out at 80° C., and as glass taps, mercury cut-offs, etc., are inconvenient at such a high temperature, a sorption balance was used. An account of a machine for winding compact silica springs has already been published.⁶ However, a sealed-up balance of the type used by McBain and co-workers⁷ would soon have become clogged with small amounts of oxides of carbon from the slow decomposition of surface oxide on the charcoal, rendering the rate of establishment of equilibrium slow. An apparatus was therefore designed so that these traces of gas would be eliminated as soon as they were formed. As this arrangement, which allows two or more samples of charcoal to be studied simultaneously, is rather novel, it is described in some detail.

The apparatus (Fig. 1) consists essentially of a water diffusion pump, a small quantity (3 grams) of water being continuously boiled in the lagged space A, and refluxed in the condenser B, so that the specimens of adsorbent in the pans C and D on the ends of the silica springs E and F are suspended in an atmosphere of water vapour at a given pressure. Owing to the slow rate of boiling and the open construction of the apparatus, the pressure was practically uniform throughout; however, the boiling was sufficiently rapid to prevent back diffusion of air into the apparatus.

It will be noticed that the steam is not condensed at the very bottom of the 4 mm. tube B, so that air would have to diffuse along some 4 cms. of narrow tubing before reaching the space O. When the external pressure is raised, it is done very slowly so that the water in A can warm up rapidly enough for its vapour pressure always to counter-balance the external pressure.

If there were no solution of air in the water as it condensed in B, a

⁵ A. S. Coolidge, *J. Amer. Chem. Soc.*, 1927, **49**, 708.

⁶ A. King, C. G. Lawson, J. S. Tapp and G. H. Watson, *J. Scientific Instr.*, 1935, **12**, 249.

⁷ J. W. McBain and A. M. Bakr, *J. Amer. Chem. Soc.*, 1926, **48**, 693.

perfect vacuum (apart from steam) would ultimately be formed round the charcoal. Actually, no doubt, a small amount of solution does occur, though the bottom of tube B behaves as a fractionating column. Since equilibrium was never apparently delayed (as compared with the rate at which it was established in an evacuated apparatus) it was thought unnecessary to sweep out the air in the apparatus with helium, which would only be dissolved to a minute extent.

The charcoal was maintained at a constant temperature in a benzene vapour jacket G, which also served to keep the water in A boiling. The bath was tested for two hours (after it had been boiling for some hours already) and showed no change on a thermometer sensitive to $1/50^{\circ}\text{C.}$; a mass of copper turnings in the bottom of G supported the inner apparatus and also prevented undue bumping. The pressure in the sorption apparatus itself was buffered by a 20 litre jar of air connected to H. Owing to the rapid setting up of equilibrium, a simple manostat, which was originally used, was found to be unnecessary.

The double surface condenser was simply made by inserting two thin quill tubes K and L inside the annular space occupied by the cooling water, the inlet tube K reaching nearly to the false bottom (which consisted of a film of sealing wax supported by a thick layer of sand). The whole benzene boiling tube was inserted in a wider tube M with mercury N at the bottom. This served both as a safeguard against fire and as an air jacket.

The suspension of the springs differed from that of previous workers in that a reference rod, hanging down the centre of the spring from the same compact support (Fig. 2), enabled the distance to be measured with the microscope to be substantially reduced. As a result, an accurate micrometer-screwed instrument could be employed. Although readings were always taken, there was no relative movement of rod and spring at the support. The readings were always repeated several times, and their average was correct to $\pm 0.01\text{ mm.}$

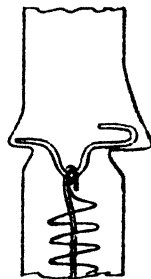


FIG. 2.

The glass pans employed were similar to those of Cameron.⁹ The charcoal had to be protected from bright light as this was observed to cause slight desorption (owing to the heating of the black charcoal).

Equilibrium was usually established within 30 to 40 minutes. Where the isotherm was steepest (large change in the amount of adsorption with a small change in water pressure), the time required was longest, up to about two hours. Initially, if the apparatus were originally full of air a few hours were necessary before the reading became constant. Owing to the thermally insulated nature of the charcoal in this type of apparatus, it is quite reasonable to suppose that the controlling factor in the establishment of equilibrium is the rate of dissipation of the heat of adsorption.

The Adsorption of Water by Charcoal.

The isotherms obtained with various charcoals are plotted in Figs. 3 and 4 on the same scale. The results are similar in character to those obtained in the presence of air, adsorption setting in at much lower pressures in the case of charcoals covered with the acidic oxide ($\text{C: } 400^{\circ}$) than with the basic oxide ($\text{C: } 850^{\circ}$), although the total adsorption at high humidities is far larger in the latter case. Thus $\text{C: } 1300^{\circ}$ finally took up over half its weight of water, yet at 50 per cent. R.H. it had adsorbed less than a totally unactivated charcoal and far less than a charcoal activated at a lower temperature. In view of the results of Langmuir⁸ who showed

⁸ A. E. Cameron, *J. Amer. Chem. Soc.*, 1931, **53**, 2646.

⁹ I. Langmuir, *J. Amer. Chem. Soc.*, 1915, **37**, 1154.

that graphite retains a surface oxide up to $1900^{\circ}\text{C}.$, this high-temperature charcoal is almost certainly covered with oxide, which must therefore be far less hygroscopic than charcoal itself, which has been studied by McBain, Porter and Sessions.¹⁰ The low-temperature acidic oxide is about equally hygroscopic as clean charcoal.

In the case of two charcoals, observations were extended so as to include a desorption curve. The hysteresis appears to be due to a variation in the nature of the surface oxide owing to its slow displacement by water. This is in accord with the work of Allmand and his collaborators.¹¹

Chemisorption of Water.

Several workers have noticed that on desorption of water from charcoal a small amount is irreversibly retained. Rakowsky¹² estimates that sugar charcoal retains 2 per cent. of its adsorbed water, some of which is not expelled on heating to redness in a current of nitrogen. Allmand,¹³ working with

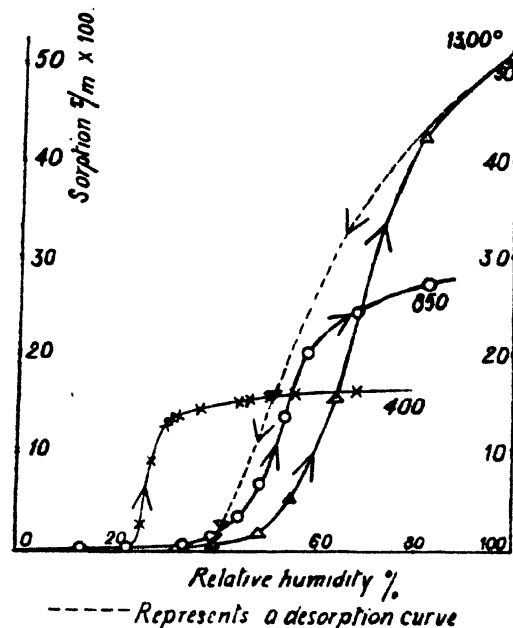


FIG. 3.—The adsorption isotherms of water on pure charcoals activated at 400° , 850° and 1300° .

wood charcoals, found that considerable and variable amounts of water were retained *in vacuo* at room temperature and that some is not desorbed even after evacuation at red heat.

The influence of such water on the properties of charcoals might be very great, so a simple experiment was carried out to measure its extent in the case of a wood charcoal and of an ash-free sugar charcoal.

The sorption balance method is insufficiently sensitive to throw any light on the question of chemisorption of water. An apparatus was therefore constructed, consisting of a 2 mm. quill tube containing 50 mgs. of water separated by a

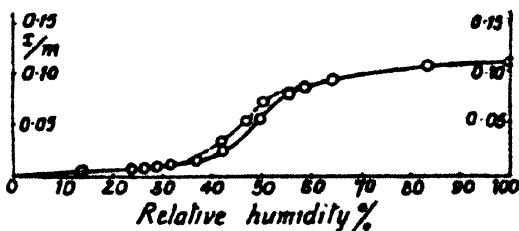


FIG. 4.—Adsorption of water on unactivated charcoal prepared at 800° ; the dotted line represents the desorption curve.

¹⁰ J. W. McBain, J. L. Porter and R. F. Sessions, *J. Amer. Chem. Soc.*, 1933, 55, 2294.

¹¹ A. J. Allmand and R. Chaplin, *Proc. Roy. Soc. A*, 1930, 129, 264.

¹² A. V. Rakowsky, *J. Russ. Physic. Chem. Soc.*, 1917, 49, 371.

¹³ A. J. Allmand, P. G. T. Hand and J. E. Manning, *J. Physic. Chem.*, 1929, 33, 1710.

diaphragm from a short wide charcoal tube. The water was outgassed and sealed up: its volume was measured by a travelling microscope, to 0.2 cu. mm. The charcoal was heated to 1300° in a crucible for a few minutes and placed in the apparatus while still warm. It was then reheated to 700° C. and sealed off whilst still red hot. The diaphragm was broken by a glass rod previously introduced into the apparatus, and the water was distilled on to the charcoal. The whole apparatus was heated to 100° C. for 2 hours and left overnight at room temperature. The water was then condensed out with solid CO₂ and the charcoal heated to 250° C. The end of the quill tube with the water was sealed off and the volume of water remeasured. The tip of the quill tube left after sealing was cooled for two hours in liquid air, but no more water condensed therein.

Sugar charcoal gave no measurable chemisorption (less than one part in a thousand) whilst birchwood charcoal retained 0.2 per cent. of its weight of water. The chemisorbed water thus seems to be attributable to the ash of the charcoal. In this respect it resembles the peroxide which can be extracted from commercial, but not from ash-free, charcoals by dilute mineral acids, after exposing them to air and water.¹⁴

The Adsorption of Water by Graphite.

There are, in general, three types of adsorption isotherm. Firstly, most of the adsorption may occur at low pressures; this is usual with charcoal. The second type, usual with glass, finely divided inert precipitates, etc., shows most adsorption at high relative humidities; this is usually due to capillary condensation. The third type is that of water on charcoal, which we have just considered. Frequently, two of these types are superimposed, as with sorption of water by textiles.

In order to determine which type of adsorption is occurring it is only necessary to determine three points on an isotherm. One point gives the scale of the curve: another at, say, 10 per cent. relative humidity shows whether or not the first type is present. Finally a further point at, say, 60 per cent. R.H. shows whether there is appreciable adsorption apart from capillary condensation.

Fifty grams of graphite - a commercial sample containing 1 per cent. of ash - in a wide vertical tube were evacuated via a three-way tap at about 10⁻⁴ mm. for two hours, the graphite being heated to 400° C. for the last half-hour (owing to a tendency of the flakes to stick together, much "boiling" occurred during this evacuation). The three-way tap was then turned and some water in the other limb was outgassed by repeated freezing and pumping. Finally, when the vacuum became hard (in the presence of a liquid air trap), the pump was turned off and the volume of water measured with a travelling microscope.

The graphite was surrounded with a Dewar flask of water at room temperature. The narrow tube containing the water was surrounded by melting ice in another Dewar. The two were then connected by the three-way tap and allowed to stand for twenty-four hours. The tap was turned off and all the water in the narrow tube driven to the bottom, where it was measured. The melting ice was replaced by cooled water at various temperatures; the Dewars always prevented a change in relative humidity of greater than 1 per cent. per hour. Since the remainder of the glass tubing was at room temperature, any condensation here was negligible.

Relative Humidity, per cent.	.	0	28	54	74	26
Adsorption $\pi/m \times 100$.	0	0.002	0.024	0.045	0.003

¹⁴ A. King and C. G. Lawson, *Kolloid Z.*, 1934, **69**, 29.

There is too much adsorption at 54 per cent. R.H. to be explained by capillary condensation, unless the capillaries approach molecular dimensions. We must therefore either reject this hypothesis, or else assume that there is some mechanism by which a large number of capillaries of the required size is produced in graphite crystals.

It is more plausible to suppose that the same mechanism exists as for adsorption by charcoal itself,¹ but that the extent of the graphite surface is far smaller.

Summary.

1. A sorption balance has been designed to measure adsorption isotherms of water on charcoal covered with various surface oxides, small quantities of desorbed gases being continuously removed.

2. Adsorption isotherms have been measured for a series of charcoals activated at different temperatures. The mean time of sojourn of water molecules on the surface of charcoal is increased by the presence of the surface oxide formed at about 400° C., and decreased by the surface oxide formed at high temperatures.

3. The extent of hysteresis is measured in the case of two charcoals.

4. When ash is present in a charcoal there may be chemisorption of water; this is not noticed with ash-free charcoal.

5. The adsorption of water on graphite is found to be of the same general type as on charcoal; the hypothesis of capillary condensation does not give a simple explanation of this fact.

In conclusion, I wish to thank the Board of Education for a grant and Mr. A. King for his interest in, and helpful criticisms of, this work.

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THE ADSORPTION ISOTHERM OF HEAVY WATER ON CHARCOAL.

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In a previous paper,¹ the fractionation of heavy water by selective adsorption on charcoal and silica gel was described. It was found that on progressive desorption of water from charcoal, the proportion of heavy water became greater until the final fraction contained about 1.4 times the amount of D₂O in the original water. Differences in the mutual polarisabilities of the two molecular species, leading to different rates of desorption, were suggested as a reason for this. In an attempt to test this hypothesis, the adsorption isotherm for pure heavy water on charcoal previously baked out *in vacuo* has now been measured, as well as a comparison isotherm for normal water under the same conditions.

The adsorptions were carried out at 110°; the rate of establishment of equilibrium was variable and never exceeded forty minutes, while twenty

¹ A. King, F. W. James, C. G. Lawson and H. V. A. Briscoe, *J. Chem. Soc.*, 1935, 1545.

minutes was adequate in some cases. This limit is probably set by the time required for thermal equilibrium which will vary very much with the method used. As in our previous work with water,² equilibrium is but slowly attained where the curve is steep. The isotherms are plotted in Figs. 1 and 2, while a comparison of the adsorption portions is shown in Fig. 3. The vapour pressure curve from which the relative humidities are calculated is that of Lewis and McDonald.³ Loss of water vapour as well as the possibility of interchange with the normal water from the air has to be avoided, and so the apparatus used for the measurement of the isotherms of water on charcoal had to be abandoned and a sealed up sorption balance used instead. Since several days elapsed before the readings were complete, there was, no doubt, a slight evolution of oxides of carbon from the charcoal or a slight reaction between it and the water, which McBain⁴ has shown to occur even at room temperature. Thus,

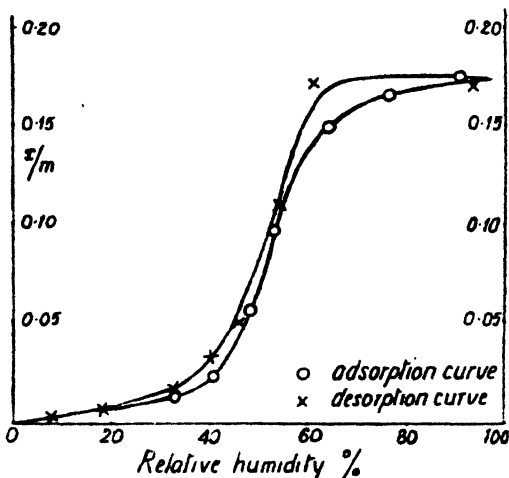


FIG. 1.—The adsorption isotherm of heavy water on outgassed charcoal at 110° .

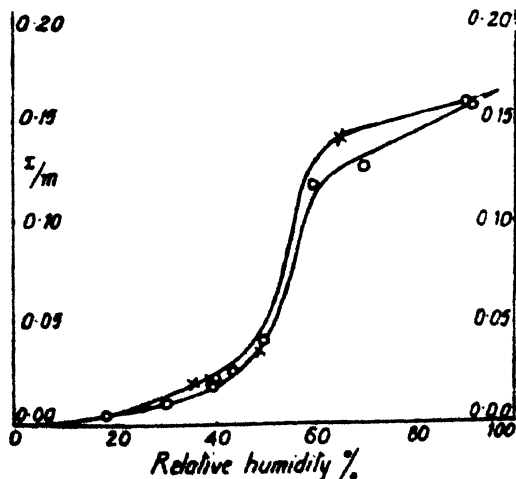


FIG. 2.—The adsorption isotherm of water on charcoal at 110° .

○ adsorption curve. × desorption curve.

extreme sensitivity of the isotherm, especially at the critical point where the adsorption increases greatly with a small increase in humidity, no

although the internal pressure after sealing the tube off from the pump was about 10^{-6} mm., it is quite likely that this had risen to 10^{-3} mm. by the time the final readings were made. In our opinion this is the reason for hysteresis which is seen to occur to a small extent, and may also account for the long equilibrium time for the steep parts of the curve.

The diagrams show that the isotherms are very similar for light and for heavy water. In view of the uncertainty of obtaining reproducible charcoal surfaces in spite of the fact that every effort was made to do so, and of the

¹ C. G. Lawson, *Trans. Faraday Soc.*, 1936, p. 477.

² G. N. Lewis and R. T. McDonald, *J. Amer. Chem. Soc.*, 1933, **55**, 3057.

³ J. W. McBain, J. L. Porter and R. F. Sessions, *J. Amer. Chem. Soc.*, 1933, **55**, 2294.

special theoretical significance can be given to the small differences between the isotherms.

In the early work on the fractional desorption of heavy water from charcoal, there was one case where some relatively heavy water appeared to be chemisorbed; the charcoal used was a commercial sample. Our

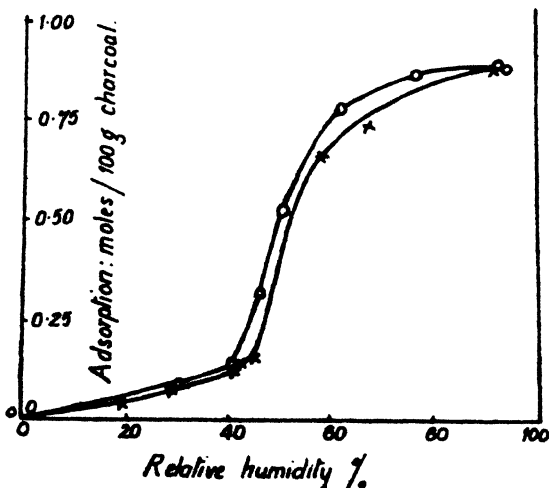


FIG. 3.—Adsorption isotherms of heavy and light water.

× light water. ○ heavy water.

more recent work has shown^a that chemisorption does not take place on a pure charcoal at low temperatures, and in commercial charcoal is associated with inorganic impurities. However, as commercial charcoals still contain a considerable amount of combined hydrogen, there is a possibility of this tending to become heavier owing to interchange between deuterium in the water and hydrogen in the charcoal. Some freshly prepared sugar charcoal which had *not* been freed from hydrogen by chlorine treatment was therefore left in heavy water for an hour at 100° C.

and then for a week at room temperature, in a sealed up, evacuated system. The water had originally been separated from the charcoal by a diaphragm and its melting-point accurately determined. After a week the water was condensed out and sealed off from the heated charcoal. Its redetermined melting-point was within 1/100° C. of the initial value, showing that if any interchange had taken place it was small, corresponding to less than 1/10,000th of the mass of charcoal.

Experimental.

Owing to the variations in the adsorption isotherm for light water on charcoal with relatively small variations in other factors, it is obviously desirable to study that of heavy water under identical conditions. The vacuum technique was therefore kept as simple as possible and was consequently not as rigorous as it might have been. A stock charcoal, activated at 400°, was used, and was not given the customary heating to a high temperature before weighing out as such heating could not be accurately reproduced. The charcoal, contained in its apparatus, was evacuated slowly and steadily to prevent "boiling," through a three-way tap, and when the vacuum had become hard was baked out for eighteen hours at 400°. By the other limb of the tap some out-gassed water was now distilled on to the charcoal, which was allowed to stand in this condition for two days during which time it was twice heated for an hour at 130°. The water was then pumped out and the temperature again raised to 400° for eighteen hours at less than 10⁻⁶ mm. pressure. No attempt was made to heat the charcoal for a limited time at a higher temperature as this led to irreproducible results. This procedure was strictly adhered to in both cases. Water (or heavy water) was then distilled into

^a See p. 477.

the apparatus, being condensed with solid CO_2 and sealed off *in vacuo* after baking the constriction. No claim is made that the surfaces of the charcoal were free from surface oxide, but the preliminary water treatment should have removed the main bulk of such oxide. The isotherms are therefore not to be compared with those of McBain⁴ who probably eliminated all traces of oxide, but rather with those of Coolidge⁵ who used a technique comparable with ours.

The apparatus (Fig. 4) consists essentially of a silica spring balance⁷ (A) kept at constant temperature and connected to a water reservoir (B) in a second thermostat at another temperature. Ebulliostatic methods were used to maintain a temperature constant to $1/50^\circ$ in a small space. The whole apparatus was contained in a tube (C) at 110° , boiling toluene at atmospheric pressure being used to maintain the temperature of the charcoal and also used to boil benzene or toluene at reduced pressure in the second thermostat (D) around the water reservoir. The same condenser (E) served for both the liquids. Owing to the compact nature of the springs, quite narrow tubing was employed, allowing room for double vapour jackets.

The pressure of the upper boiling liquid was buffered by a 20 litre jar of air, connected to an accurate mercury manometer. As equilibrium was quickly established at 110° actual manostats were unnecessary. A test showed that the temperature of the inner vapour jacket was constant within 0.01° for several hours, even when the temperature of the outer bath was varied between 4° and 20° above the boiling-point of the upper boiling liquid, and the flow of water in the condenser was altered within wide limits.

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⁴ A. S. Coolidge, *J. Amer. Chem. Soc.*, 1927, **49**, 708.

⁷ A. King, C. G. Lawson, J. S. Tapp and G. H. Watson, *J. Scientific Instruments*, 1935, **12**, 249.



[heat]
FIG. 4.

THE RATES OF INTERACTION OF PROTO- AND DEUTERO- HYDROGEN AND METHANE WITH CHARCOAL.

BY RICHARD M. BARRER, PH.D., M.Sc.

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In a recent communication from this laboratory,¹ a study of the interactions of methane and hydrogen with carbon showed that with either gas an atmosphere of hydrogen resulted, and that a two-dimensional surface hydride of carbon was formed. Only at higher temperatures and pressures of hydrogen could any synthesis of methane be

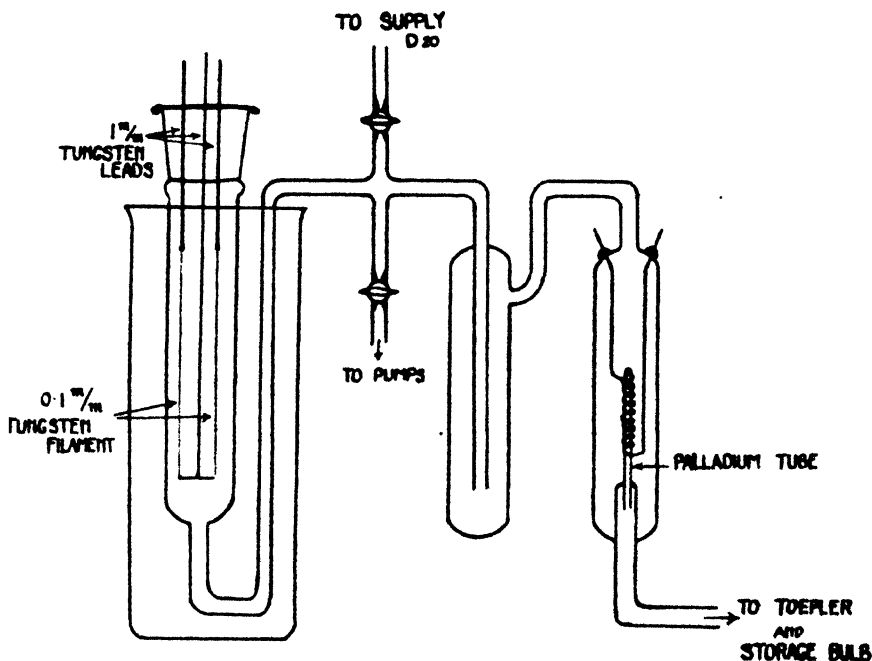
¹ Barrer and Rideal, *P.R.S.*, 1935, 231; Barrer, *P.R.S.*, 1935, 253.

detected, and this synthesis was extremely slow. The adsorption was very energetic, isotherms at different temperatures indicating a heat of about 50 Cals. for the chemisorption of hydrogen, while the energy of activation on one sample showed a variation with the degree of saturation of surface of from 10 to 30 K. Cals. from 0 to 20 per cent. saturation. Both reactions are suited to the study of the relative velocities of reaction of proto- and deuterio-molecules. Three sources of differing reaction rate may be anticipated, due to mass variation, zero-point energy differences, and different permeabilities towards energy barriers.

The first effect will not be large with CH_4 and CD_4 molecules, since $\sqrt{\frac{M_{\text{CD}_4}}{M_{\text{CH}_4}}} = 1.12$. Both the reactions involve proton exchange, which can include permeability effects.

Experimental.

The apparatus used in the chemisorption of hydrogen and methane has been described elsewhere (ref. 1). Deuterium was prepared in the



PREPARATION OF DEUTERIUM

FIG. 1.

apparatus of Fig. 1. A little heavy water vapour was admitted to a tungsten filament (thoroughly out-gassed at 2300° K. for several hours) and the filament was then burned at red heat in the water vapour, so that deuterium was liberated. The resultant gases were then passed through a U-tube immersed in liquid air, and were allowed to diffuse through a palladium tube heated to 700° K. The effluent gas was collected and stored by means of a Toepler pump. Methane and deuterio-methane were prepared from light and heavy water and aluminium carbide, and the velocity sorption checked against pure methane from another source to test its purity.

Results.

(a) The Activated Sorption of Hydrogen and Deuterium.

The activated adsorption rates of the hydrogens were studied over as wide a temperature interval as possible (500°-900° K.) on a sugar carbon of 0.01 per cent. ash content. Pressure-Time curves gave the retardation in sorption velocity already observed (Barrer¹), even at low concentrations of hydrogen. Sorption rates were compared by commencing experiments with equal samples of each gas, and drawing tangents to Log_{10} (Pressure)-time curves at points of equal adsorption. Typical results are given in Table I. In all the experiments 4.1 grammes of carbon were used, and check experiments made to show that no change in the adsorbent had taken place.

TABLE I.—TEMP. 696° K.

C.C. Gas Sorbed at N.T.P. 105.	$\frac{\partial}{\partial t} \log (p_i - p_s)$ k_{H_2}	$\frac{k_{H_2}}{k_{D_2}}$	$\frac{\partial}{\partial t} \log (p_i - p_s)$ $= k_{D_2}$	$\frac{k_{H_2}}{k_{D_2}}$	$\frac{\partial}{\partial t} \log (p_i - p_s)$ $= k_{H_2}$
30.0	0.186	1.74	0.109	1.60	0.171
47.0	0.138	1.85	0.075	1.61	0.120
53.5	0.117	1.78	0.064	1.65	0.105
57.0	0.090	1.76	0.051	1.68	0.086
60.0	0.083	1.76	0.047	1.71	0.080
62.4	0.073	1.79	0.040 ₈	1.73	0.070 ₈
63.4	0.068	1.75	0.038 ₈	1.77	0.068 ₈
64.0	0.066	1.83	0.035 ₈	1.83	0.065 ₈
65.2 (when sorption complete.)					

Although the value of $\frac{\partial}{\partial t} \log (p_i - p_s)$ decreases continuously the ratio of the expression for hydrogen and deuterium remains constant for stages where equal amounts of gas are adsorbed. The deuterium samples employed were 80-60 per cent. pure, since an 80 per cent. heavy water was employed in their preparation. As reaction proceeded isotopic fractionation by reaction occurred, and over the later stages of the reaction substantially pure deuterium was being chemisorbed. Thus the ratio of the rates became constant over the final stages of chemisorption, and only the ratios in this reaction region were employed in subsequent calculations. Table I. shows a quite large difference the reaction in velocities at a given temperature. Table II. shows how the ratio of reaction velocities varied as a function of temperature.

TABLE II.

Temperature °K.	890	698	603	585	500
Ratio of velocities.	1.44	1.77	1.84	1.94	2.37

As the temperature decreased the ratio increased. This is in accordance with differences in rate of reaction due to zero point energies, but not in accord with differences caused by effusion processes. At the same time the possibility of both these processes occurring simultaneously has to be considered. A conclusion on this point may be arrived at as follows. Reaction proceeds at any instant according to an expression

$$-\frac{dp}{dt} = k(p_i - p_s)e^{-\frac{E}{RT}} \quad . \quad . \quad . \quad . \quad (1)$$

so that $-\frac{d \ln(p_i - p_e)}{dt} = K e^{-\frac{E}{RT}} = k_i$ at constant temperature. For the reaction involving the hydrogen isotopes we may write

$$r = \frac{K_{H_2}}{K_{D_2}} = e^{-\frac{(E_{H_2} - E_{D_2})}{RT}} = \frac{\frac{d}{dt} \cdot \{\ln(p_{H_2} - p_{e,H_2})\}}{\frac{d}{dt} \cdot \{\ln(p_{D_2} - p_{e,D_2})\}} \quad (2)$$

as given for example in Table I.

Hence
$$\frac{\partial}{\partial \frac{1}{T}} \cdot \log r = -\frac{(E_{H_2} - E_{D_2})}{2.303R} = -\frac{\Delta E}{2.303R} \quad (3)$$

Equation (3) is a general differential equation which will give a family of particular solutions of which two cases may apply:

$$2.303 \log r = -\frac{\Delta E}{RT} \text{ (without effusion)} \quad (4)$$

and

$$2.303 \{\log r - \log \sqrt{2}\} = -\frac{\Delta E}{RT} \text{ (with effusion)} \quad (5)$$

The general equation (3) was first used to determine ΔE by plotting $\log r$ as a function of $1/T$. The value thus obtained was 780 Cals. Now in Table III. are given the values of ΔE calculated from equations (4) and (5) respectively:—

TABLE III.

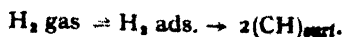
Temp. °K.	Ratio (Equation 4).	ΔE Cals.	Ratio 1.414 (Equation 5.)	ΔE Cals.
890	1.44	650	1.02	33
698	1.77	800	1.25	315
603	1.84	740	1.30	310
585	1.94	800	1.37	310
500	2.37	865	1.68	706
		Average 700		

Obviously equation (5) disagrees with equation (3), nor does it give constant ΔE values, where-

TABLE IV.

Amount Sorbed c.c. at N.T.P. $\times 10^3$.	Velocity Constant at 696° K.	Velocity Constant at 603° K.	Apparent Energy of Activation, cals./gram. mol.
30.0	0.186	0.0342	15,700
44.0	0.138	0.0194	17,900
53.5	0.117	0.0137	18,700

as there is good agreement between (4) and (3). Thus diffusion in the bulk phase or on the surface does not combine with the chemical process as a rate determining step in the temperature range studied. The molecules of hydrogen and deuterium react according to the scheme:



and there is a preliminary van der Waals adsorption sufficiently rapidly established to maintain the surface concentration at its equilibrium value.

The apparent energy of activation for the chemisorption of hydrogen on charcoal F is shown in the following data to be initially about 15,000 cal./gram. mol., and to increase steadily as the amount of gas sorbed increases.

TABLE V.

Temperature °K.	K_{CH_4}	K_{CD_4}	Ratio.
83S	—	0.044	—
	0.086	—	1.66
	—	0.059	—
920	0.156	—	—
	—	0.080	1.52
	0.090	—	—
950	0.381	—	—
	—	0.270	1.44
	0.381	—	—

(b) **Chemisorption of Light and Heavy Methane by Carbon.**

The sorption data for methane were treated in a similar manner to those for hydrogen. The results are given in Table V.

From Table V. one can calculate the zero-point energy differences needed to explain the different reaction rates:—

Temperature °K.	83S	920	950
Zero point energy difference (calories)	880	770	700

The apparent energy of activation² for the chemisorption of methane on carbon F is given by the data here shown.

Temp. °K.	Velocity Ratio $\frac{CH_4}{CD_4}$	Energy K Cals.
838-950	4.44 —	26.7
838-950	— 5.22	31.4

Discussion.

It is of importance to note that ΔE remains constant down to 500° K. At this temperature, according to some recent work,³ one would expect that effects due to tunnelling would intervene. This would

² This energy is so much lower than the value *ca* 53 K. Cals. observed on another charcoal, C. (ref. 1) as to suggest that the gas prepared from carbide and employed in these chemisorptions might not be methane but hydrogen. Consideration of the actual velocity constants for chemisorption of hydrogen and of methane on the two carbons C and F gave the following relationship:

$$\begin{aligned} \frac{A_{H_2} - \text{Carbon C}}{A_{H_2} - \text{Carbon F}} &\sim \frac{1}{4} \\ \frac{A_{CH_4} - \text{Carbon C}}{A_{CH_4} - \text{Carbon F}} &\sim \frac{1}{100} \end{aligned}$$

The velocities and energies of activation of hydrogen sorption on both carbons were comparable, but there seems something specific in the increase in K and decrease in E for carbon F. To show that the gases employed were methanes, a comparison was made of the sorption rates of the gas from aluminium carbide, hydrogen, and pure methane from another source. The results are as shown.

³ Bell, *P.R.S.*, 1933, 139A, 466; Bawn and Ogden, *Trans. Faraday Soc.*, 1934, 30, 432.

Temp. °K.	K (Hydrogen.)	K (Gas from Carbide.)	K (Methane).
940	—	0.381	—
	—	—	0.300
	—	0.380	—
860	0.502	—	0.330
	—	0.096	—
	0.532	—	—

cause an apparent increase in ΔE which is not realised in the experiment. One thus finds that quantum mechanical effects of the type indicated are absent in a reaction which should be very favourable to their occurrence. The magnitude of ΔE is that encountered in other heterogeneous processes, such as the diffusion of hydrogen through palladium⁴ (830 Cals.) or the hydrogenation of ethylene by nickel⁵ (700 Cals.).

Summary.

(1) The relative rates of sorption of proto- and deuterio-molecules of hydrogen and methane on carbon indicate zero-point energy differences of 770 and 750 Cals. respectively.

(2) The hydrogen sorption showed no tunnelling mechanism down to 500° K., and no mass factor in the constant A of the equation

$$\frac{(\text{rate})_{\text{H}_2}}{(\text{rate})_{\text{D}_2}} = Ae^{-\frac{\Delta E}{RT}} \text{ so that } A = 1.$$

The ratio of the velocities decreased in both sorptions as the temperature increased.

I wish to thank Professor E. K. Rideal, F.R.S., for his continued interest in the work, and the 1851 Commissioners for an Overseas Scholarship.

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⁴ Farkas and Farkas, *Proc. Roy. Soc.*, 1934, 144A, 467.

⁵ Melville, *J.C.S.*, 1934, 797.

THE INTERACTION OF LIGHT AND HEAVY WATER WITH ALUMINIUM CARBIDE AND CALCIUM PHOSPHIDE.

BY RICHARD M. BARRER, PH D., M.Sc.

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In a paper on the chemisorption of light and heavy hydrogens and methanes by carbon¹ it was shown that the differences in rate of sorption had all the properties of differences due to zero point energies. The differences, when expressed as,

$$\frac{k_{\text{H}_2}}{k_{\text{H}_1}} = Ae^{-\frac{\Delta E}{RT}},$$

gave a value of $A = 1$.

ΔE was constant between 500° and 900° K., and no penetration of energy barriers could be detected. If reactions could be studied which

¹ Barrer. This volume, p. 481.

proceed at room temperatures, an enhanced separation in the velocity constants might occur, and would imply quantum mechanical effects of the type discussed among others by Bell² and Bawn and Ogden.³

Many measurements of heterogeneous processes have shown that a ΔE due to zero point energy differences may be set at 600-900 Cals., with considerable certainty, but a value of ΔE , as calculated from the above equation of about 2000 Cals. would at low temperatures imply tunnelling through energy barriers. A test of this could be made by observing $\frac{\partial(\Delta E)}{\partial T}$ which should decrease rapidly with increasing temperature

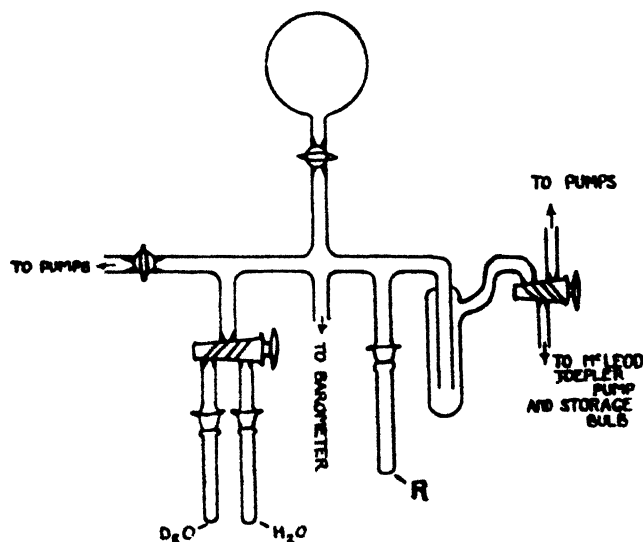
until a constant value of ΔE , due to zero point energy difference only, was observed.

Reactions which proceed readily at room temperatures are the decomposition with water of aluminium carbide and of calcium phosphide with liberation of methane and of phosphine respectively. It has been stated⁴ that at 80° C. the ratio $\frac{k(\text{H}_2\text{O}-\text{Al}_4\text{C}_3)}{k(\text{D}_2\text{O}-\text{Al}_4\text{C}_3)}$ was 23, a value suggesting a tunnelling process. Another method which did not, however, eliminate the possibility of exchange reactions, gave a separation factor of only two.⁵

Experimental.

The apparatus employed in the decomposition of carbide and phosphide is shown in Fig. 1.

By manipulation of the two-way tap the light or heavy water (98 per cent. D content) could be distilled on to the carbide or phosphide. These had both been heated and thoroughly out-gassed under high vacuum, and during the distillation were immersed in liquid air. When the temperature was brought to room temperature reaction proceeded and the velocities were



APPARATUS FOR DECOMPOSITION
CARBIDES, PHOSPHIDES AND NITRIDES

FIG. 1.

followed by means of McLeod gauge or barometer.

The amounts of material and of liquid water was such that during

² P.R.S., 1933, 139A, 466.

³ Trans. Faraday Soc., 1934, 30, 432.

⁴ Urey and Price, J. Chem. Physics, 1934, 2, 300.

⁵ Hughes, Ingold and Wilson, Nature, 1934, 133, 291.

reaction no appreciable decreases in the weight of either occurred. Under these conditions a zero order process was obtained. When an experiment was completed the light or heavy water was again brought back to the

TABLE I.

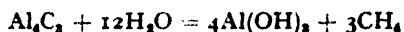
Exp.	<i>t</i> (mins.).	<i>p</i> (cms. $\times 10^3$).	<i>p/t</i> ($\times 10^4$).	Temperature °K.
1	39	6.70	1.73	273
2	38	5.00	1.32	273
3	40	4.80	1.20	273
4	22	11.5	5.23	287
5	28	3.9	1.40	273
6	18	11.0	6.11	287
7	37	5.95	1.61	273

show that the carbide or phosphide was of unchanged reactivity. The reaction with calcium phosphide was so vigorous that water vapour only could be used in the reaction. The two-way tap was opened and water vapour allowed to enter the evacuated system containing phosphide. This vapour then decomposed the phosphide.

The phosphide used was a commercial sample. The carbide was made by heating aluminium powder and carbon in an electric furnace *in vacuo* (thereby avoiding contamination by aluminium nitride).

Results.

The reaction



was studied between 273° and 293° K. A large number of experiments were made with light water to determine the temperature coefficient of the reaction. A sequence of these experiments is given in Table I.

TABLE III.

$\text{D}_2\text{O}..$	$\text{H}_2\text{O}.$	$\text{D}_2\text{O (Check).}$
$\frac{\Delta p}{\Delta t} = K_{\text{D}_2\text{O}}.$	$\frac{\Delta p}{\Delta t} = K_{\text{H}_2\text{O}}.$	$\frac{\Delta p}{\Delta t} = K_{\text{D}_2\text{O}}.$
0.0137	0.051	0.0121
0.0127	0.054	0.0124
0.0133	0.052	0.0123
0.0159	—	—
0.0148	0.050	0.0132
0.0141 Average	0.052 Average	0.0125 Average

these results should be more accurate. The following results were obtained at 273° K. (Table III.).

tubes H_2O or D_2O with liquid air. The method allowed the same samples of carbide and phosphide to be used with both heavy water and light water, without destroying either. This avoided the variability encountered with different samples even of the same batch. Control experiments were made throughout to

TABLE II.

Temperature Range.	Temperature Coefficient.	Apparent Energy of Activation. (Cal. mol.).
273-287	3.90	15,200
273-288.6	4.15	14,200
273-292.2	5.45	13,900
273-291.7	4.85	13,500
		Average 14,200

Similar series of experiments were conducted between 273 and 288.6, 292.2, 291.7° K., and in Table II. are collected the temperature coefficients and an apparent energy of activation calculated therefrom.

The particular point of interest is the possibility of repeating the large separation in reaction velocity (23 : 1 at 353° K.) reported by Urey and Price.⁴ Since the same sample of carbide was used with both light and heavy water and control experiments performed

From Table II. $\frac{k_{\text{H}_2\text{O}}}{k_{\text{D}_2\text{O}}} = 3.9$ at 273°K . We may conclude from this small ratio that no tunnelling through an energy barrier is involved, whilst the difference in zero-point energy needed to give the observed separation

is 750 Cals. Since $\sqrt{\frac{D_2\text{O}}{H_2\text{O}}}$ is nearly unity mass differences are insignificant.

The reaction of water vapour with powdered calcium phosphide according to the equation

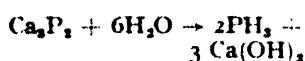


TABLE IV.

Exp. No.	Time (mins.).	PH_3 Press. (cms. Hg.).	Water Used.	Temperature $^\circ\text{K}$.
1	15	0.92	D_2O	290
2	15	1.08	H_2O	290
3	15	0.91	D_2O	290
1	10	1.08	H_2O	291
2	10	0.89	D_2O	291
3	10	1.18	H_2O	291

is limited by the rate at which diffusion can occur, and by the relative vapour pressures of light and heavy water (about 10 : 9 at room temperature ⁶). Table IV. shows the results of a set of experiments.

It was also shown that, when the vapour pressure of the water was constant, and the temperature of the phosphide was raised, the reaction velocity did not increase more than would conform to a \sqrt{T} diffusion in the material (Table V.).

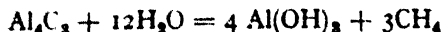
TABLE V.

Exp. No.	Time (Mins.)	PH_3 Press. (cms. Hg.).	Temperature $^\circ\text{K}$.
1	10	0.89	290
2	10	0.94	311
3	11	1.00	290
4	10	1.08	325
5	11	0.88	290

Discussion.

The decomposition of calcium phosphide by water vapour is an example of a chemical process controlled by a non-activated

diffusion. It is impossible to control decomposition by liquid water. The much slower carbide reaction is governed by a chemical process without evidence of a superposed diffusion. In the carbide lattice are two kinds of aluminium atom plane and two kinds of carbon atom plane per lattice layer.⁷ Thus there may be different types of aluminium-carbon bond, and one cannot assign the activation energy to any particular type. The heat of the reaction



is 352 K. Cals.⁸ Therefore, the average energy per C—H bond formed is 28 K. Cals., compared with what may be an average energy of activation per C—H bond formed of 14 K. Cals. That no process ascribable to tunnelling of energy barriers could be observed suggest that the barriers are much wider than thought at present, or that present-day calculations do not yet include all the important factors.

⁶ Lewis and MacDonald, *J.A.C.S.*, 1933, **55**, 3057.

⁷ Stackelberg and Schnorrenberg, *Z. physik. Chem.*, 1934, **27B**, 37.

⁸ Terebesi, *Helv. Chim. Acta*, 1934, 819; Internat. Critical Tables.

Summary.

(1) The decomposition of aluminium carbide by liquid water has an apparent energy of activation of 14 K. Cals. The reaction rates for light and heavy water are as 3.9 : 1 at 273° K., corresponding to a zero-point energy difference of 750 Cals. There is no evidence of a tunnelling mechanism at 273° K.

(2) The decomposition of calcium phosphide by water vapour is governed by a diffusion process. At constant water vapour pressure the temperature coefficient is very small. The rates of decomposition by light and heavy water vapour are in the ratio of the vapour pressures of light and heavy water.

I am indebted to Professor E. K. Rideal for discussion and encouragement, and to the 1851 Commissioners for an Overseas Scholarship.

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THE THERMAL DECOMPOSITION OF LIGHT AND HEAVY AMMONIA AND PHOSPHINE ON TUNGSTEN.

BY RICHARD M. BARRER, PH.D., M.SC.

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The decomposition of ammonia on tungsten filaments has been studied by various workers,¹ between 2 and 500 mm. pressure. The reaction has not been adequately examined at low pressures. Schwab's² work is confined mainly to the decomposition on platinum. The decomposition of phosphine on tungsten was studied by Melville and Roxburgh.³ Both these reactions were re-examined, using proto- and deuterio-molecules, mainly at low pressures. The determination of zero point energy differences on a number of tungsten catalysts was not however the only reason for pursuing the investigations. There exists a wide discrepancy in recorded energies of activation for the seemingly simple zero order ammonia decomposition. These energies range from 26 to 47 K. Cals. One can conclude either that the methods of measurement are inadequate, or that the activation energy varies in a random manner from one tungsten catalyst to another. The latter consideration seems unlikely in view of the stability of a polycrystalline tungsten filament when outgassed at 2000° C. We have therefore measured the energy of activation by the compensating filament method.⁴ This was done for both the phosphine and the ammonia reactions and trustworthy energies of activation were obtained. If a number of true energies of activation (*i.e.*, for the zero order reactions)

¹ Hinshelwood and Burk, *J.C.S.*, 1925, 127, 1105; Kunsman, *J.A.C.S.*, 1928, 50, 2100; Hailes, *Trans. Faraday Soc.*, 1931, 27, 601; Moteschan, *Perevesen-seff Roginsky Acta Physicochimica*, 1935, 2, 203.

² Schwab, *Z. physik. Chem.*, 1927, 128, 161.

³ *J.C.S.*, 1933, 586.

⁴ Forsythe and Worthing, *Astrophys. J.*, 1935, 61, 146.

can be measured, absolute rates can be calculated, just as for homogeneous processes. The well-known characteristics of polycrystalline tungsten filaments⁵ enabled the calculations to be made for the two reactions here studied.

Experimental.

The reactions occurred on tungsten filaments of lengths 31 and 9 cms. and of 0.1 mm. diameter. Each filament during reaction formed one arm of a Wheatstone's bridge. The bridge was kept in balance, and the catalyst so maintained at constant temperature, by increasing the total current through the bridge as the reaction proceeded. From the properties of ideal filaments,⁶ the temperature could be calculated for a given filament current *in vacuo*. In the presence of the gas the current was increased until the resistance (and therefore temperature) of the filament was that already measured *in vacuo*. The cooling effect of the 1 mm. tungsten lead was allowed for by calculation as suggested by Langmuir, MacLane and Blodgett.⁷ This does not yet allow the true temperature coefficient to be measured however. The velocity on the short filament at temperature T_1 was next subtracted from the velocity on the long filament at T_1 . The resultant velocity was taken as representing the velocity on the middle section (22 cms.) of the long filament. This resultant velocity was used to determine energies of activation.

Light and heavy ammonias and phosphines were prepared from magnesium nitride, and calcium phosphide, previously outgassed, in an apparatus described elsewhere.⁸ The D-content of ammonia was estimated from vapour pressure measurements, and of phosphine from density measurements. 98 per cent. D_2O was used in preparing ND_3 and PD_3 . Ammonia and phosphine were purified by distilling several times between liquid air and solid carbon dioxide. Hydrogen was prepared electrolytically, and passed over palladium-coated copper at $350^\circ C$. and phosphoric oxide. Cylinder nitrogen (99 per cent. pure) was passed over palladium-coated copper at $350^\circ C$. and through a liquid air trap. The filaments were thoroughly outgassed (several hours at $2000^\circ C$.) before use, and were also outgassed between each experiment for 20 minutes at the same temperature. Under these severe conditions the catalytic activity was reasonably constant. After an experiment with ammonia a filament retained occluded gas, which with for an initial gas pressure 10^{-2} cm. was comparable in amount with this pressure. The phosphine decomposition gave negligible occlusion. This suggests that the occluded gas was nitrogen. For the phosphine decomposition a stoichiometric relation held between initial and final volumes as demanded by the equation $2PH_3 = 2P + 3H_2$, the phosphorous being deposited as the red variety on the glass walls. The ammonia decomposition was more complicated. More gas was obtained finally than the original pressure indicated. This was traced to a strong and relatively slow sorption⁹ by the walls of the reaction vessel. Typical of this sorption are the data here shown.

Ammonia was therefore admitted at a higher pressure than that at which the experiment was subsequently conducted, until the sorption was nearly completed. Some was then frozen out, a convenient pressure obtained, and after a further interval for desorption the run was commenced.

$Cms. \times 10^3$ Press. NH_3	Time (Mins.)
2	0
1.2	1
0.85	2.5
0.65	4.0
0.50	5.5
0.43	7.0

⁵ Becker, *Rev. Mod. Physics*, 1935, 7, 95.

⁶ Langmuir, *Physic. Rev.*, 1916, 7, 154; *ibid.*, 1916, 7, 302.

⁷ *ibid.*, 930, 35, 478.

⁸ Barrer. This volume, p. 487.

⁹ Cf. Burt, *Trans. Faraday Soc.*, 1932, 28, 179.

Kinetics of the Reactions.

The ammonia decomposition was studied between 6.1×10^{-4} cms. and 6.3×10^{-3} cms. pressure. The reaction is nearly of zero order, except at the highest temperatures (Table I.) and lowest pressures, on the 9 cm. filaments.

Similarly at the lower temperatures (ca 900° K.) at which measurable

TABLE I.

Time Mins.	Total Press. $\times 10^3$ cms.	$K = \frac{\Delta p}{\Delta t} 10^3$.
---------------	------------------------------------	--

Temp. 1060° K.

0	6.60	
1	7.15	0.55
2	7.64	0.49
3	8.24	0.60
4	8.60	0.30
5	9.18	0.58
6	9.68	0.50

Temp. 1174° K.

0	10.0	
1	15.26	5.26
2	18.85	3.59
3	21.30	2.45
4	22.55	1.25

TABLE II.

Initial Press. (cms. $\times 10^3$).	$\frac{(dp)}{(dt)_{\text{init.}}} \times 10^3 = k$ (t in mins.)
0.61	0.37
0.96	0.52
3.00	0.62
5.35	0.64
10.0	0.97
14.5	0.83
15.0	0.93
19.9	0.86
25.0	1.00
33.0	1.00
63.6	0.96

decomposition occurred on the longer 31 cm. filaments, a good approximation to zero order was again found (Fig. 1). A feature of the reaction was the occurrence of a zero order velocity constant at 6.1×10^{-4} cms. pressure of only 0.37 times the velocity constant at pressures of 10 to 60×10^3 cms. Also decomposition occurred with an initial pressure of 6.1×10^{-4} cms. until 7×10^{-3} cms. pressure obtained in the gas phase. Both these effects

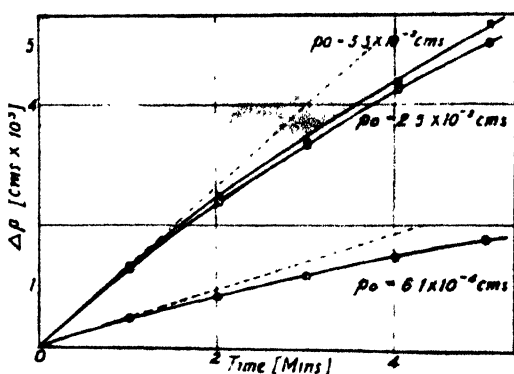


FIG. 1.

were ascribed to sorption on the walls. The walls by giving off ammonia as that in the gas phase was decomposed, acted as a reservoir of ammonia which kept the gas phase and therefore filament surface concentrations nearly constant and so gave the appearance of a zero order reaction on the filament, which could yet be less rapid than the true zero order process at greater pressures. On this basis the relation between the initial value of dp/dt and

the pressure should be that of an isotherm, of which the initial curvature is controlled by the sorption isotherm of ammonia on glass, and of which the last portion is controlled by the saturation concentration at the tungsten surface. The relevant data, collected in Table II., and Fig. 2, show that this is indeed the case :

Over a sixteen-fold increase in pressure there was a 2.5-fold increase in velocity, and then above about 10^{-2} cms. the velocity remained constant.

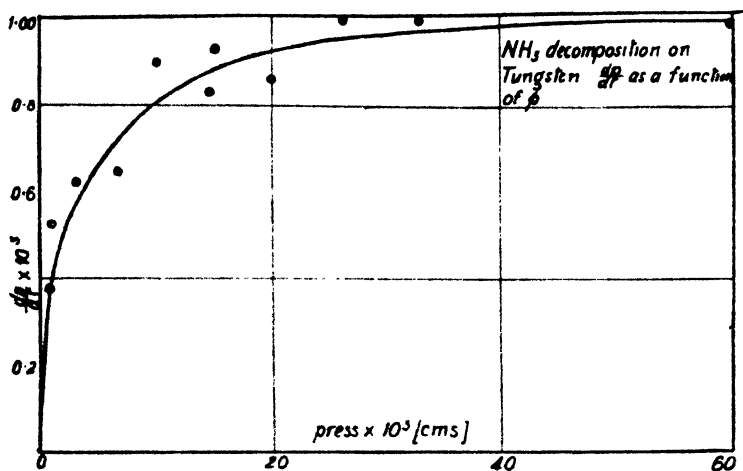


FIG. 2.

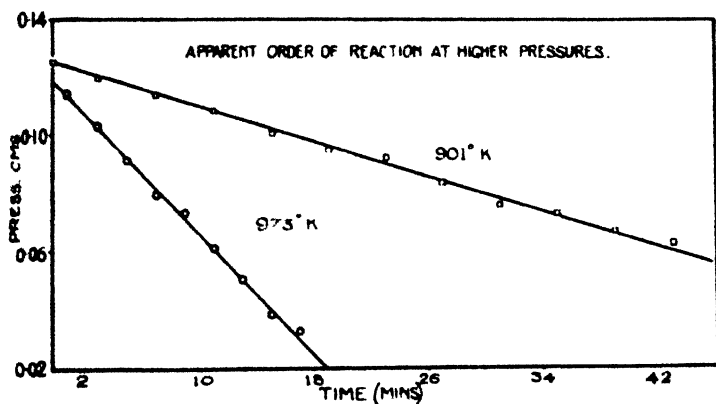


FIG. 3

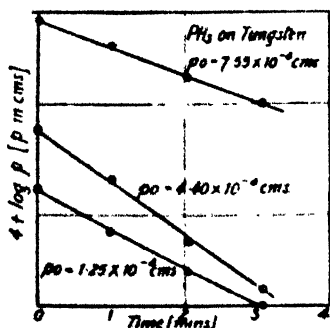


FIG. 3a.

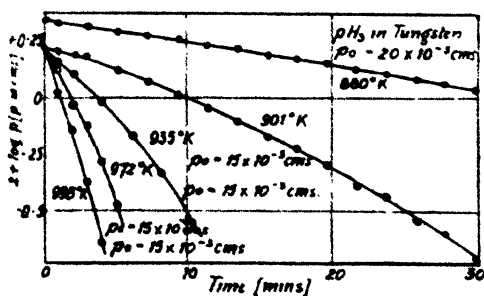


FIG. 3b.

The kinetics of phosphine decomposition were not complicated by sorption on the walls and enabled an interesting change in the order of the reaction with varying pressure to be followed.

On a 31 cm. filament between 10^{-4} and 10^{-3} cms. pressure Fig. 3a shows that a first order reaction was obtained. On a 9 cm. filament at pressure

TABLE III.

Time Mins.	Press. PH_3 (cms. $\times 10^3$).	k from Eqn. (1).	Time from Eqn. (2), (Mins.).
0	23.07	—	0
5	20.07	4.0	4.5
9	18.51	3.1	9.7
13	16.97	3.4	13.0
21	13.57	3.3	21.2
31	10.23	—	30.5
41	7.11	3.3	41.0
51	4.89	3.2	50.9
61	3.07	—	61.9

(15 to 20) $\times 10^{-3}$ cms. pressure the plot of Log (press.) against time was definitely curved, showing a reaction of intermediate order (Fig. 3b). Finally at pressures of a few millimetres a zero order reaction was found (Fig. 3c). The kinetic equation for the reaction

of intermediate order, at 860° K. was either

$$-dp/dt = k p^{\frac{1}{2}} \quad (1)$$

$$\text{or, } -dp/dt = ap/1 + bp \quad (\text{with } a = 0.0227 \text{ and } b = 26.60). \quad (2)$$

as is shown by the data of Table III. The rate equation thus follows a Freundlich or a Langmuir isotherm.

The most interesting way to follow the transition from first to zero order is by measuring the half-life period as a function of pressure. At low pressures the half-life ($t_{\frac{1}{2}}$) should be independent of pressure, and at high pressures proportional to it. These predicted relations are realised in the data of Table IV.

The experiments establish that the real rate determining process is unimolecular with respect to phosphine. Fig. 4 shows the relation between the half-life period and the pressure at two different temperatures, on a 9 cm. filament.

TABLE IV.

Press $\times 10^3$ (cms.).	$t_{\frac{1}{2}}$ (mins.).	$\frac{t_{\frac{1}{2}}}{p} \times 10^3$.
9 cm. filament 972° K.		
127.9	10.4	0.000
32.7	4.05	0.124
17.4	2.90	0.167
10.2	2.26	0.222
4.39	1.81	0.413
1.03	1.62	1.00
0.83	1.30	1.58
0.44	1.10	2.50
0.189	1.10	5.82
31 cm. filament ° K.		
81.5	8.88	0.109
74.5	8.80	0.118
16.6	4.60	0.277
9.9	3.30	0.330
9.8	3.35	0.328
9.5	3.40	0.368
5.0	2.40	0.480
4.0	2.10	0.520
1.74	2.25	1.29
0.76	2.20	2.92
0.44	1.60	3.64
0.245	1.30	5.30
0.123	1.50	12.20

Energetics of the Reactions.

The velocity of thermal decomposition of ammonia on 9 and 31 cm. filaments was measured over a range of temperatures. Excellent linear graphs of Log (k) against $\frac{1}{T}$ ($T = ^\circ\text{K.}$) were obtained. The slope for the 9 cm. filament is greater than for the 31 cm. filament, the apparent energies being respectively 52.3 and 43 K. Cals. The corresponding rate equations are:

$$\text{Log}_{10} K_1 = 7.409 - \frac{52,300}{2.303RT} \quad (1)$$

$$\text{Log}_{10} K_1 = 6.475 - \frac{43,000}{2.303RT} \quad (2)$$

From the linear graphs of $\text{Log } K$ against $1/T$, the value of $K_1 - K_2$ was obtained at two different temperatures. The integrated van't Hoff isochore

$$\text{Log}_e \frac{(K_1 - K_2)_{T_1}}{(K_1 - K_2)_{T_2}} = \frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

then gave the true value of E for the zero order reaction as 42,400 cal./gram. mol. for 22 cms. of the central zone of the 31 cm. filament. The true rate equation is then

$$\text{Log}_{10} (K_1 - K_2) = 6.35 - \frac{42,400}{2.303RT}$$

The energy of activation for the decomposition of phosphine was calculated from the relationship between the half-life period ($t_{1/2}$) and the

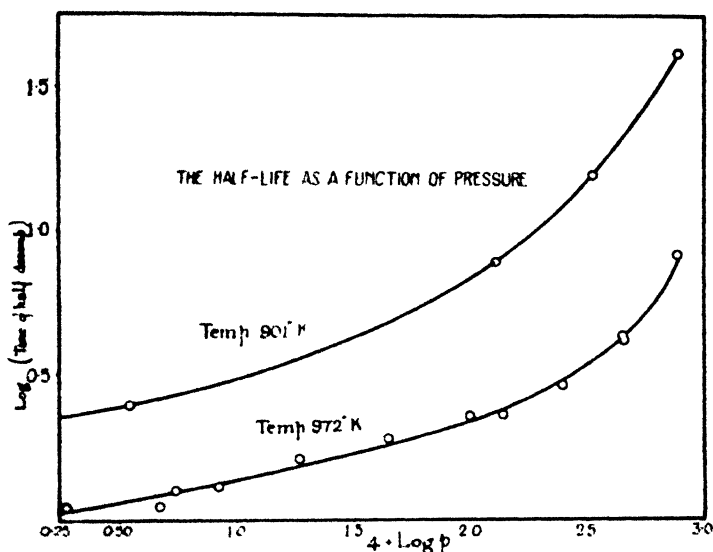


FIG. 4.

temperature, and also from the value of dp/dt at constant pressure and at various temperatures. The temperature coefficient was not the same at all pressures for a given rise in temperature. The relationship between derived energies of activation E_1 and E_2 for the reaction proceeding as a first and an apparent zero order reaction respectively is $E_1 + \Delta H_s = E_2$, where ΔH_s is the heat of sorption of the phosphine on tungsten. The values of E as a function of pressure are given in Table V.

TABLE V.

9 cm. filament.

 $T_1 = 401^\circ \text{ K.}$ $T_2 = 972^\circ \text{ K.}$

Press. (cms. $\times 10^3$).	$(t_{1/2})_{T_1}/(t_{1/2})_{T_2}$	$E(\text{K. Cals.})$	$\left(\frac{dp}{dt}\right)_{T_1}/\left(\frac{dp}{dt}\right)_{T_2}$	$E(\text{K. Cals.})$
0.23	—	—	3.0	26.6
0.47	2.74	24.6	—	—
8.00	—	—	3.7	32.0
14.00	3.60	31.3	—	—
18.00	—	—	3.6	31.3
34.00	3.86	33.0	—	—
127.00	3.99	34.2	—	—

Similarly for a 31 cm. filament between 878.8° K. and 919.2° K. the following values were obtained :

Press (cms. 10 ³).	E (K. Cals).
0.41	26.5 (First Order Reactions)
9.0	31.5 (Intermediate Order)
80.0	32.5 (Approximate Zero Order)

From the differences in the extreme values of E of 10 and 6 K. Cals. for the 9 and 31 cm. filaments one can assume ΔH_a to be about 8 K. Cals. The rate equations are :

$$\text{Log} \left(\frac{dp}{dt} \right)_1 = 5.69 - \frac{32,500}{2.303RT},$$

and

$$\text{Log} \left(\frac{dp}{dt} \right)_2 = 5.39 - \frac{32,500}{2.303RT},$$

for the long and the short filaments respectively. From these relations when $\text{Log } dp/dt$ is plotted as a function of $1/T$ the true energy of activation may be derived, since

$$\frac{\partial}{\partial T} \left[\text{Log} \left\{ \left(\frac{dp}{dt} \right)_1 - \left(\frac{dp}{dt} \right)_2 \right\} \right] = \frac{E_{\text{true}}}{2.303R}.$$

From the values of dp/dt at 800° and 900° K., and employing the integrated isochore one obtains.

$$\text{Log} \frac{0.00273}{0.000274} = \frac{E_{\text{true}}}{2.303R} \left(\frac{1}{800} - \frac{1}{900} \right),$$

whence $E = 32,200$ Cals.

The Influence of Products upon the Velocity of Decomposition.

It has been shown that hydrogen has no effect upon the decomposition of phosphine.⁹ It has been stated by Schwab² that the ammonia decomposition is retarded by the resultants, whereas Hinshelwood Burk and Hailes¹ consider the reaction to be unretarded, in spite of a known strong sorption of hydrogen by clean tungsten,¹⁰ or of the possibility of nitriding of the filament. A new series of experiments was carried out on the influence of hydrogen, nitrogen and oxygen on the ammonia reaction. In an orienting experiment the filament was heated in ammonia at 1700° K. until the latter was decomposed. Residual hydrogen, nitrogen and ammonia were pumped off, but the filament was not outgassed, and retained occluded gases. A subsequent experiment at 984° K. gave the same velocity of decomposition as did the outgassed filament. The wire (0.1 mm diameter and 31 cms.

TABLE VI.

Initial Pressure of Gas 10 ³ (cms.)	Reaction Velocity.
Hydrogen.	
0	0.82
6.6	0.94
11.4	0.98
16.5	1.00
17.9	1.03
23.5	0.88
30.4	1.00
Nitrogen.	
0	0.75
13.6	0.78
28.7	0.91

long) gave off 0.25 c.c. of gas at N.T.P. when it was subsequently glowd at 2200° K. Thus occluded gas has no influence. Further investigation

¹⁰ Roberts, *Proc. Camb. Phil. Soc.*, 1934, 30, 1/4.

was carried out by adding various initial pressures of hydrogen and nitrogen and observing the decomposition velocities. The results of Table VI. show that these gases had no observable influence.

Oxygen on the other hand produced definite retardation. Ammonia was admitted, and the run commenced at 975°K. , the usual zero order reaction being obtained. The ammonia was frozen out, and the oxygen at 2×10^{-3} cms. pressure admitted to the filament at 600°K. and then pumped off. The original

experiment was then recommenced the value of dp/dt being first negligible and then increasing steadily towards the original value, apparently due to a process of clean-up of the oxygen film which restored the original catalytic surface. Finally the experiment was repeated with some gaseous oxygen present. dp/dt was now no longer positive (*i.e.*, an increase in

total pressure with time) but negative.¹¹ The results are summarised in Fig. 5. It is of interest that the effect of oxygen is not permanent at 975°K.

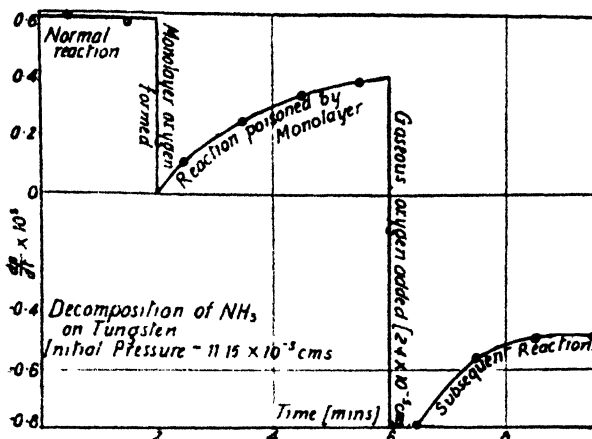


FIG. 5.

TABLE VII.

CATALYST A. 9 CM. FILAMENT. 0.1 MM. DIAM.
TEMP. 1085°K.

$dp/dt \times 10^3$. (NH_3 , 70% H, 30% D.) $dp/dt \times 10^3$. (ND_3 , 98% D.)

0.72	0.51
0.63	0.53
0.70	0.54
0.64	0.49
—	0.52
0.67	0.52

were prepared. These were decomposed on three catalysts A, B, C. The results of a number of the experiments are summarised in Tables VII., VIII., IX.

For the gases of the compositions of the Table VII., a difference in zero point energy ΔE of 550 cal./mol. will give the observed separation. Assuming a linear relation between D-content and ΔE , the ΔE for pure NH_3 and ND_3 is 800 cal./mol.

For catalyst B, $\Delta E \approx 790$ cal./gram. mol. for the pure gases ND_3 , NH_3 .

Relative Velocities of Decomposition of Proto- and Deutero-Molecules.

Three samples of ammonia of D-contents 98 per cent., 30 per cent. and 0 per cent.

TABLE VIII.

CATALYST B. 31 CM. FILAMENT. 0.1 MM. DIAM.
TEMP. 956°K.

$dp/dt \times 10^3$. (NH_3 , 100% H.)	$dp/dt \times 10^3$. (NH_3 , 98% D.)
0.285	0.173
0.370	0.250
0.270	0.208
0.312	0.210

¹¹ Pressures were measured with a Macleod gauge, so that water vapour pressures are not given adequately.

For Catalyst C, $\Delta E = 890$ cal./gram. mol. for the pure gases. The values of

TABLE IX.

CATALYST C. 31 CM. FILAMENT. 0.1 MM. DIAM.
TEMP. 990° K.

$dp/dt \times 10^3$, (NH ₃ , 100 % H.)	$dp/dt \times 10^3$, (ND ₃ , 90 % D.)
0.71	0.57
0.88	0.52
0.92	0.53
0.84	0.54

ΔE agree with the experimental errors with each other, and the value 900 cal./gram. mol. given by Taylor and Jungers at much higher pressures.¹² It is of importance to note that ΔE is constant within the errors of experiment for a surface process wherein various tungsten catalysts were employed.

Experiments were made on similar lines with PH₃ and PD₃. The separations encountered were smaller. Values of dp/dt were derived from pressure-time curves, and, as for ammonia, the relation

$$\text{Log} \left(\frac{dp}{dt} \right)_{\text{PH}_3} / \left(\frac{dp}{dt} \right)_{\text{PD}_3} = \frac{\Delta E}{RT}$$

was used to calculate ΔE . The results of numerous experiments on two different catalysts D and E are summarised in Tables X. and XI. Again both catalysts D and E gave the same separation ΔE of 550 cal./gram. mol. for pure PH₃ and PD₃.

TABLE X.—CATALYST D. 9 CMS. LONG. 0.1 MM. DIAM. PH₃ AND PD₃ (98 PER CENT. D CONT.).

Press. $\times 10^3$.	$dp/dt \times 10^3$.		Ratio.	Temp. °K.	ΔE (Cals.)
	PH ₃ .	PD ₃ .			
12	0.238	—	1.42	860	600
	0.252	0.173			
9.5	—	0.400	1.38	901	590
	0.595	—			
	—	0.420			
	—	0.416			
	0.550	—			
8.5	—	0.420	1.32	936	520
	—	0.692			
	0.935	—			
9.5	—	0.729	1.25	973	490
	2.53	—			
	—	2.07			
	2.62	—			

Mean Value, $E = 550$ Cals.

¹ Taylor and Jungers, *J.A.C.S.*, 1935, **57**, 679.

TABLE XI.—CATALYST E. 31 CMS. LONG. 0.1 MM. DIAM. PH₃ AND PD₃ (80 PER CENT. D).

Press. $\times 10^3$ (cms.).	Ratio $\frac{dp}{dt} \text{PH}_3 / \frac{dp}{dt} \text{PD}_3$.	Temp. °K.	Mean E (Cals.) for 100 Per Cent. PD ₃ .
9 7 5	1.27, 1.27 1.24, 1.29 1.23, 1.31	873	490
9 7 5	1.42, 1.62, 1.34, 1.43 1.53, 1.47, 1.34, 1.57 1.27, 1.32, 1.20, 1.43	836	500
9 7 5	1.34, 1.25, 1.40 1.20, 1.27, 1.34 1.20, 1.37, 1.36	819	510

Mean Value, $\Delta E = 510$ Cals.

Discussion.

Since hydrogen has no influence upon the reaction rates for either phosphine or ammonia, it is improbable that the evaporation of a tungsten hydride layer is a rate determining step. Since, however, proto- and deuterio-molecules do not decompose equally fast, in both reactions rearrangement of hydrogen bonds is involved. Thus evaporation of tungsten-nitride or a tungsten-phosphorus layer is not a rate controlling step. For the phosphine decomposition our experiments establish that the rate determining step is a true first order reaction; and the same is most probably true of the ammonia decomposition.

The simplest theory supposes that the energy is communicated by the underlying solid. Then:

$$\text{Rate} = No. (p \cdot \nu) \cdot e^{-E/RT} \quad (1)$$

Where $No.$ = the number of molecules adsorbed/cm.² and ν has the dimensions of a frequency, and is often identified with the characteristic frequency of the solid. The factor p allows for deactivation before reaction, and for the participation of many degrees of freedom in supplying the activation energy (*cf.* Eqn. (2)). More explicitly¹³ the equation becomes:

$$\text{Rate} = No. f(E_1, n) \frac{\alpha}{\beta} \cdot \nu \cdot e^{-E/RT} \quad (2)$$

Here $f(E_1, n)$ expresses the effect of n degrees of freedom on the rate, α is the rate at which the preactivated molecules become critically activated and decompose, supposing no deactivation occurred and β is the rate at which deactivation takes place. $f(E_1, n) \geq 1$; $\alpha/\beta \leq 1$. The transition state method¹⁴ gives the rate as:

$$No. \cdot C \cdot F'_a/F_n \cdot KT/h \cdot e^{-E_a/RT} \quad (3)$$

¹³ Hinshelwood, *J.C.S.*, 1935.¹⁴ Tolman "Statistical Mechanics; Chem. Cat. Co." 1927, Eyring, *J. Chem. Phys.*, 1935, 3, 107 *et al.*

C is the reciprocal of the number of times the activated state must be crossed before reaction occurs. F'_a and F_n are partition functions for the activated and normal states respectively. F'_a however does not include the partition function of the co-ordinate in which decomposition occurs. The partition function of this co-ordinate is included in the factor $KT/h \cdot e^{-E_a/RT}$. T has the maximum rates, at the temperature $\approx 1000^\circ \text{K.}$, according to (1), (2); and (3) respectively¹⁵ equal to

$$5 \times 10^{12} \cdot e^{-E/RT} \quad \text{and} \quad 2 \times 10^{13} \cdot e^{-E_a/RT},$$

where the E 's are not defined in quite the same way;

$$E = E_0 + \Sigma [f \cdot (\nu' T)] - RT,$$

if E is obtained from the expression $\partial/\partial T \cdot \log(\text{rate}) = E/RT^2$. In what follows we shall neglect $\Sigma [f(\nu' T)]$. Also ν in (2) is taken as equal to the lattice frequency of tungsten.

At saturation $No = 7.0 \times 10^{14}$ mols./cm.² (one PH_3 or NH_3 molecule per two W atoms). The ratio 1.4 : 1 gives the ratio of real⁸ to apparent surface.

The rate constants at 1000°K. and at 900°K. for the ammonia and phosphine decompositions are respectively 1.34×10^{-3} cms./minutes and 2.73×10^{-3} cms./minute. Equation (1) gives a value of $p = 10^{-3}$ and 1.4×10^{-4} for the ammonia and phosphine decompositions respectively (assuming $\nu = 5 \times 10^{12}$). On the basis of equation (2) this is to be interpreted as a small ratio α/β . When $\nu = KT/h = 2 \times 10^{13}$, and $E = (E_0 - RT)$, as in the equation (3) the values of $p = C \cdot F'_a/F_n$ become 2×10^{-4} and 3×10^{-5} for the ammonia and phosphine decompositions respectively. A restriction on the validity of these calculations is the assumption of a uniform catalytic activity of the surface.¹⁶

It is interesting to collect the energies of activation recorded for each reaction in the series (see table on opposite page).

The most uncertain method of measuring filament temperature seems to be direct determination of resistance, which often gives much lower energies than do measurements by other means.

Summary.

1. The thermal catalytic decomposition of ammonia on tungsten filaments has been studied between 6×10^{-1} and 6×10^{-4} cms. pressure at temperatures between 950° and 1150°K. The thermal catalytic decomposition of phosphine has been studied between 10^{-1} and 2×10^{-4} cms. pressure, and from 800° to 970°K. On various tungsten catalysts the ammonia decomposition was over early stages a zero order reaction. Towards the end of decomposition, or at the lowest pressures the velocity fell as the ammonia pressure decreased. The kinetics of decomposition of phosphine could be followed from a first order reaction at pressure 10^{-4} to

¹⁵ This calculation assumes that F'_a/F_n has the value unity, and that $p = f(E_1, n) \frac{\alpha}{\beta}$ of equations (1) and (2) have the value unity. Often these quantities are less than unity, $f(E_1, n)$ can however be greater than unity.

¹⁶ Roberts work (*P.R.S.*, 1935, 152A, 445) suggests that after strong outgassing ($> 2000^\circ \text{K.}$) and then exposure to residual gas from the walls of the apparatus, about 12 per cent. of the tungsten atoms only should remain denuded of oxygen under the conditions of our experiments. The remaining 88 per cent. very quickly takes up a stable atomic film of oxygen.

Worker.	Reaction.	Energy of Activation. (Cals.).	Temperature Measurement.
Hinshelwood and Burk	NH ₃ Decom- position	38.7 (zero order)	Resistance.
Taylor and Jungers	"	35.0 " "	"
Kunsman	"	47.3 " "	Optical Pyrometer
Hailes	"	40.31 " "	Resistance
Perevessenseff, Motscham and Roginsky	"	42.1 " "	Optical Pyrometer
Barrer	"	42.4 " "	Current-Temperature. Characteristics of ideal filaments and compensating fila- ment method.
Melville and Roxburgh	PH ₃ Decom- position	25 (Inter. Order)	Compensating fila- ment method
Barrer	"	25 (First order) 32.2 (Approx. zero order)	Compensating filament method.

5.0×10^{-3} cms., to an intermediate order reaction from 10^{-3} to 5×10^{-3} cms., and an approximate zero order reaction at pressures ca 10^{-1} cms.

2. The rate determining step in both reaction involves a rearrangement of a hydrogen bond, since separations were observed in zero-point energy of 800 to 900 Cals. in the case of proto- and deutero-ammonia, and 550 Cals in the case of proto- and deutero-phosphine. The rate determining step in the phosphine decomposition is unimolecular.

3. Hydrogen and nitrogen have no influence upon the velocity of catalytic decomposition of ammonia. Oxygen-treated catalysts are temporarily poisoned but recover their activity at least in part as the reaction proceeds. The presence of a little gaseous oxygen alters the nature of the decomposition at 1000° K.

4. Energies of activation were measured by a compensating filament method which eliminates the effect of end losses. The energy of activation for the zero order ammonia decomposition was 42.4 K. Cals, and for the first order phosphine decomposition 25 K. Cals. The zero order phosphine decomposition gave an energy of activation of 32.2 K. Cals. Calculations were made of the absolute rates, which were respectively $\frac{1}{1000}$ and $\frac{1}{7000}$ for the ammonia and the phosphine decompositions, of the rate given by

$$- \frac{du}{dt} = N_0 \cdot v_0 e^{-E/RT}.$$

It is a pleasure to thank Professor E. K. Rideal, F.R.S., for his interest and advice, and the 1851 Exhibition Commissioners for an Overseas Scholarship.

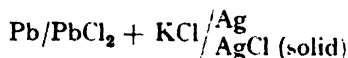
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A THERMODYNAMIC STUDY OF SYSTEMS OF THE TYPE $\text{PbCl}_2\text{--KCl--H}_2\text{O}$ AT 25°C . PART V.

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In Parts I.¹ and II.² of this series, the results of measurements of E.M.F. at 25°C . on cells of the type



were described, the values of $[\text{PbCl}_2]$ and of $[\text{KCl}]$ being varied independently over the complete concentration range up to saturation. It was shown that, by suitable application of the Gibbs-Duhem equation³

$$N_1 d \ln a_1 + N_2 d \ln a_2 + N_3 d \ln a_3 = 0$$

to the experimental results, the values of a_2 and of a_3 could be calculated for all solutions in equilibrium with the three solid phases PbCl_2 ; PbCl_2 , KCl , $1/3 \text{H}_2\text{O}$; and 2PbCl_2 , KCl , utilising the a_1 values given by the electrometric data, and taking the value of a_2 for a saturated KCl solution (free from PbCl_2) from the work of others. In a liquid phase containing PbCl_2 , a_2 cannot be directly determined, but, on the other hand, a_3 is given by the relative aqueous vapour pressure of the solution. Such measurements therefore not only can be used to check the values of a_2 calculated for the saturated solutions mentioned above, but also, when applied, in conjunction with the known a_1 values, to unsaturated solutions, or to solutions in equilibrium with solid PbCl_2 , will permit of the calculation by the Gibbs-Duhem equation of the value of a_2 in such solutions. The work described in this paper was undertaken with these two ends in view. The working out of the experimental technique took a considerable time, as did the measurements themselves. In addition, curious anomalies were encountered with solutions in the neighbourhood of 0.8N . KCl , the same region in which the E.M.F. and phase equilibrium data had also proved difficultly reproducible.⁴ The upshot was that, except in this region, no results with unsaturated solutions were obtained.

Apparatus.

We required a method capable of giving vapour pressures to an accuracy of 0.1 per cent., *i.e.* in our case, to about 0.02 mm. of mercury. Methods which could not be used in presence of a solid phase were inadmissible, and methods involving prolonged boiling of the solution to remove dissolved air were ruled out, in view of possible disturbance from hydrolysis of PbCl_2 . Direct methods, depending on the lowering in height of a barometric column of mercury, were dismissed as not being capable of the

¹ *Trans. Faraday Soc.*, 1927, **23**, 470.

² *Ibid.*, 1933, **29**, 679.

³ N_1, N_2, N_3 and a_1, a_2, a_3 refer to the molar numbers and activities of PbCl_2 , KCl and H_2O respectively, the a values all being taken as unity for the pure condensed phase.

⁴ *Ref.* 2, p. 680.

requisite accuracy, apart from minor objections, and the differential pressure method perfected by Lovelace, Frazer and Sease³ was clearly too laborious in view of the large number of data required. This limited us, at that time, to the use of a dynamic or streaming technique, and we finally settled on the recently devised method of Pearce and Snow,⁴ which promised both the required accuracy and relatively easy and rapid manipulation.

In this method, a stream of electrolytic gas is passed at a constant rate of flow, controlled by an ammeter, through a series of saturators of special design, immersed in a thermostat and containing the solution under experiment. The aqueous vapour is caught in absorption tubes and weighed. From the number of mols. of electrolytic gas passed, exactly known by including a silver coulometer in the electrolysis circuit, the weight of water carried forward, and the barometric pressure, the vapour pressure of the solution is calculated by direct application of Dalton's Law. We employed essentially the apparatus as described by Pearce and Snow, introducing one or two modifications found by experience to give more certain and reproducible results. The **electrolysers**, six in number, were connected in series with an adjustable resistance, an ammeter and the 100-volt D.C. main. A coulometer could be included in the circuit as and when desired. Each consisted of a 3-litre wide-necked bottle, charged with 25 per cent. NaOH, and closed by a cork driven flush with the top level of the bottle, through which passed the gas outlet and two conical ebonite bushes which carried the electrodes. After filling and inserting the cork, the whole was sealed by a thick cap of paraffin wax. The electrodes were vertical concentric cylinders of nickel gauge, 4.5 inches high and 2.3 inches in diameter, their edges being rivetted by nickel wire into slots cut in $\frac{1}{4}$ -inch nickel rods, which passed through the ebonite bushes mentioned above. A tubular glass separator prevented any possibility of chance contacts between the electrodes.

The **coulometer** consisted of a 150 c.c. platinum crucible, in which was suspended a pure silver rod anode, surrounded by a porous alundum cup. The composition and purity of solution, current density, etc., were in accordance with the usual standard specifications. The combined output of the electrolysers passed along a delivery tube, where its pressure was measured by a **water U-manometer**, through a **regulating tap**, to the barrel of which was sealed a long glass arm to ensure accurate setting, and to the **pre-saturator**. This was about 10 inches long, and of the pattern designed by Bichowsky and Storch⁵ and used by Pearce and Snow. It was charged with water, and kept at a steady temperature between 25°-27° by electrical heating, the whole being lagged with asbestos wool. The gas current, supersaturated with aqueous vapour, then passed to a battery of eight further **saturators** of the same type as the pre-saturator, arranged in series in a thermostat at 25°. The first seven contained the solution under investigation and the last was empty. Slight condensation of water took place in the first saturator, equilibrium was finally adjusted in numbers 2-7, and the absence of any trace of liquid deposit in 8 at the end of a run was looked on as showing that no spray was being carried forward.

The gas finally emerged through a vertical tube from the end of the last saturator. This was electrically heated above water level to 40°-50° C. to prevent any possible loss of water by condensation, and terminated in a mercury-seal cup, to which the **absorber** was connected. This contained glass wool, cut into short lengths, and coated with P_2O_5 by shaking the two materials together. The packing had the advantages of large absorbing surface, lightness and negligible resistance to flow. The original pattern of U-tube absorber used was modelled on that of Pearce and Snow. Occasional difficulty when filling, owing to P_2O_5 getting between the sides of

³ *J. Amer. Chem. Soc.*, 1916, **38**, 515.

⁴ *J. Physic. Chem.*, 1927, **31**, 231.

⁵ *J. Amer. Chem. Soc.*, 1913, **37**, 2696, Fig. 2.

the U and the tap barrels, led to its replacement by one closed by ground glass caps fitting *over* cones ground on the *outsides* of the limbs of the U. The apparatus train terminated in a **guard tube** containing P_2O_5 .

The most important modification in the apparatus as compared with that of Pearce and Snow was the introduction of the regulating tap and manometer. With the electrolyzers connected directly on to the pre-saturator, it was found impossible to obtain a steady rate of flow of gas through the saturators, the gas tending to bubble out through the apertures on the lower side of the inclined tubes, instead of passing up inside the latter. By working with a steady pressure of about 20 cm. of water inside the electrolyzers, this trouble was completely avoided, and a smooth flow of the required rate obtained. The gas pressure in the saturators themselves was of course not affected by this procedure.

A few other points of practical interest may be briefly mentioned. (i) The actual rate of flow was limited by the capacity of the coulometer and by the necessity of avoiding any spray production. A current of 0.35–0.4 amp. was found suitable under our conditions. (ii) The optimum temperatures of the pre-saturator ($25^\circ\text{--}27^\circ\text{C}$.), and of the exit tube from the saturators ($40^\circ\text{--}50^\circ\text{C}$.) were worked out from experience. In the latter case, too high a temperature was found to lead to mercury being carried forward from the mercury seal into the absorber, whilst too low a temperature resulted in excessive condensation of moisture in the side arm of the latter. (iii) The packing of the absorber required care. If done too tightly, the increased resistance to gas flow caused a rise of pressure above atmospheric in the last saturator (the method of calculation assumes this to be one atmosphere) leading to low results. Any such effect was made evident by rises in pressure in the mercury seal and in the gas-generator manometer. It was only once experienced during the work. Towards the end of the experiments, a small manometer tube sealed into the cap on the filler of the last saturator, gave direct evidence that the pressure inside the latter was atmospheric. (iv) When filling the saturators with solution at 35° (see later), there was a tendency towards formation of a condensed film of moisture on their upper inside surfaces whilst cooling to 25° . Until this had been swept away by the stream of gas, the measured vapour pressures naturally tended to be high, subsequently falling to the correct value. In practice, the trouble was readily avoided by tilting the saturators to and fro after filling.

Experimental Procedure.

The heating currents were switched on and the cleaned and dried saturators placed in the thermostat and connected up. Pure water was put in the pre-saturator. Some 600 c.c. of the solution under examination were prepared at $60^\circ\text{--}70^\circ$ by the addition of the requisite amounts of KCl and PbCl_2 (analytical reagents) to boiled out distilled water. When using solutions saturated with PbCl_2 or one of the double salts, about 20 per cent. of PbCl_2 over and above that required to form the actual saturated solution at 25°C . was used. After cooling to 35° , the solution was charged into saturators 1–7, the last being left empty. Residual solution was kept in a vessel in the thermostat, and subsequently analysed. The absorber was filled, air dried by passage over 1 m. of CaCl_2 , followed by 1 m. of P_2O_5 , drawn through it for thirty minutes,* the absorber then cleaned by wiping and hung with a suitable counterpoise in the balance case. The platinum dish of the coulometer was cleaned, heated to 150° , and cooled in a desiccator. The electrolyzers were switched on, without the coulometer in circuit, and gas passed through the saturators overnight.

On the following day, absorber and platinum dish were weighed, the coulometer assembled, the absorber fitted with the guard tube and,

* Preliminary experiments showed both that the air stream was sufficiently dried and that no P_2O_5 was carried forward in this process.

simultaneously, the coulometer switched into the circuit and the absorber attached to the mercury seal of the outlet from the saturators. A run lasted five hours. Every hour the barometer was read to 0.1 mm., and its pressure corrected to 0° C. and 45° latitude. At the end of the run, absorber and coulometer were simultaneously removed. Dry air was sucked through the former for thirty to forty minutes, thus replacing the electrolytic gas, and carrying forward on to the P_2O_5 , any moisture condensed in the side-tube. Absorber and counterpoise were then wiped clean, hung in the balance case, and weighed an hour later and on the following day. The solution was siphoned off from the platinum dish, the deposit washed with distilled water subsequently siphoned off, the dish heated to 150°, cooled in a dessicator, and weighed an hour later and on the next day.

The vapour pressure of the solution p is given by the expression

$$p = P \times \frac{\text{mols. water vapour}}{\text{mols. water vapour plus mols. hydrogen and oxygen}}$$

where P is the corrected atmospheric pressure. Inserting the electrochemical equivalent of silver, this becomes

$$p = P \times \frac{w_{H_2O} \cdot 18.016}{\frac{w_{H_2O}}{18.016} + \frac{w_{Ag}}{23.973}}$$

where w_{H_2O} and w_{Ag} represent the increase in weight of absorber and coulometer dish respectively.

Results.

Table I. contains the results of measurements with pure water, with saturated solutions of KCl free from $PbCl_2$,

TABLE I.

Expt	Grams KCl per 1000 grams H_2O .	Grams $PbCl_2$ per 1000 grams H_2O .	p (mm.).	p/p_0 .
1	0.0	0.0	23.78	1.0000
2	0.0	0.0	23.78	
3	0.0	0.0	23.79	
4	Saturated— not analysed	0.0	20.13	
5		0.0	20.11	—
68	361.1 (Saturated)	0.0	19.99	0.8406
69		0.0	20.08	0.8444
70		0.0	20.06	0.8436
73		0.38	23.40	0.9840
75	40	0.0	23.43	0.9853
75	58	0.50	23.15	0.9735
76	58	1.00	23.25	0.9777
72	58	1.71	23.73	0.9979
71	58.76	1.84	23.34	0.9815
77	59	1.0	23.19	0.9752
74	60	0.85	23.77	0.9996

The relative pressures in the last column, as in the next Table, are calculated on the basis of the figure for p_0 of 23.78 mm. obtained in Expts. 1 and 2.

Table II. contains the results of measurements on solutions saturated with a solid phase containing $PbCl_2$.

Discussion.

In Fig. 1 the results of Table II. are plotted in the form of relative pressures against KCl molality, whilst Fig. 2 contains the data^a up to

^a All molalities mentioned in the text refer to KCl.

TABLE II.

Expt.	KCl Molarity.	Solid Phase.	p (mm.).	p/p_0 .	Expt.	KCl Molarity.	Solid Phase.	p (mm.).	p/p_0 .
6	0.0	PbCl ₂	23.75	0.9987	52	0.791	PbCl ₂ + 2PbCl ₂ KCl	23.67	0.9954
7			23.71	0.9971	53			23.23	0.9767
19			23.59	0.9920	54			23.20	0.9756
20			23.60	0.9924	28			23.17	0.9743
10	0.0981		23.50	0.9907	29	0.802	PbCl ₂ + 2PbCl ₂ KCl	23.20	0.9756
11			23.40	0.9865	32			23.07	0.9701
12			23.45	0.9861	07			23.10	0.9714
13			23.44	0.9857	30			23.14	0.9730
21	0.204		23.42	0.9849	31	1.016	2PbCl ₂ KCl	23.06	0.9697
22			23.41	0.9844	33			23.01	0.9676
17			23.36	0.9823	34			22.99	0.9668
18			23.38	0.9832	30			23.04	0.9689
8	0.404		23.35	0.9819	40	1.210	PbCl ₂ KCl	23.03	0.9685
9			23.37	0.9828	37			22.78	0.9580
26			23.31	0.9804	38			22.82	0.9596
27			23.35	0.9810	04	22.54	0.9479		
15	0.530		23.27	0.9786	05	1.313	PbCl ₂ KCl	22.50	0.9500
16			23.29	0.9794	41			22.48	0.9453
14			23.27	0.9786	42			22.50	0.9462
47			23.58	0.9916	35			22.46	0.9445
48	0.571		23.29	0.9794	36	1.812	PbCl ₂ KCl, 1/3 H ₂ O	22.48	0.9453
49			23.73	0.9979	63			21.80	0.9167
50			23.59	0.9920	55			21.33	0.8970
51			23.76	0.9991	50			21.40	0.8999
23	0.740		23.24	0.9772	57	3.17	PbCl ₂ KCl, 1/3 H ₂ O	21.39	0.8995
24			23.20	0.9781	61			21.13	0.8886
25			23.27	0.9786	58			20.94	0.8806
43			23.75	0.9987	62			20.46	0.8604
44	0.701		23.74	0.9983	59	4.40	PbCl ₂ , KCl, 1/3 H ₂ O + KCl	20.04	0.8427
45			23.77	0.9996					
46			23.73	0.9979					
66			23.79	1.00					
	0.782								

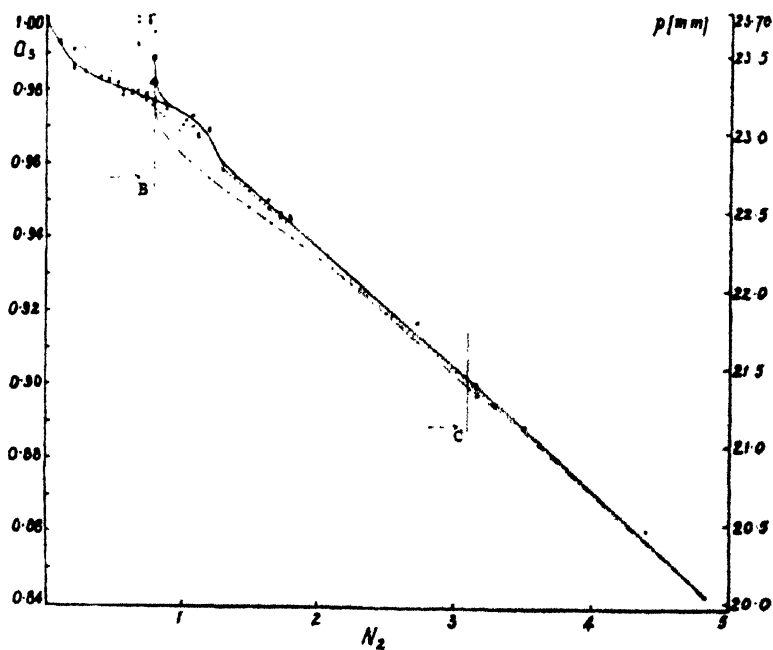


FIG. 1.

1.1 *M.* plotted on a larger scale. The dotted curves are the relative vapour pressure curve for solutions of KCl free from PbCl_2 , plotted from the concordant data of Lovelace, Frazer and Sease,¹⁰ Pearce and Snow,⁶ and Hepburn.¹¹ The chain curve represents, down as far as 0.791 *M.* (point B—invariant point with PbCl_2 and 2PbCl_2 , KCl as solid phases), the relative vapour pressures of the saturated solutions actually dealt with in this paper, as calculated in Part II. We should expect our own points to fall on this curve, which is clearly not the case. The concentration range 0.678–0.791 *M.*, inside which were observed the abnormally high vapour pressures italicised in Table II., obviously requires separate discussion. Apart from these experiments, inspection of the Table shows that, out of eighteen solutions on which two or more measurements were made, in ten cases the figures differed by 0.02 mm. or less, this being the standard we originally aimed at; whilst in four instances (at 0.204, 1.088, 1.65 and 3.17 *M.*) the discrepancies exceeded 0.04 mm. In two of these cases, extra measurements indicated one of the two discordant values to be the more probable. On seven solutions, one measurement only was made. Examination of Fig. 1 suggests that, in two of these cases (2.74 and 4.40 *M.*) the observed values were too high by perhaps 0.10 and 0.06 mm. respectively, but that the other measurements were of a much higher degree of accuracy.

Omitting these two doubtful values from consideration, it appears that, starting with the most concentrated solution (in equilibrium with both KCl and PbCl_2 , KCl $1/3 \text{ H}_2\text{O}$) and passing towards more dilute solutions, there is very little difference between calculated and observed values up to near the invariant point C (solid phases PbCl_2 , KCl, $1/3 \text{ H}_2\text{O}$ and 2PbCl_2 , KCl). The concentration here is 3.096 *M.*, and the calculated value of a_2 0.8995. Table II. shows this to be one of the values actually obtained at 3.17 *M.*; the difference between found and calculated values in this region would be about 0.04 mm., the former being the higher figure. From this point down to 1.812 *M.*, there are unfortunately no experimental points available for comparison, no weight being laid on the single determination at 2.74 *M.*, as has already been mentioned. The course of the experimental curve from this concentration onwards appears reasonably well defined; it would seem to run above the curve

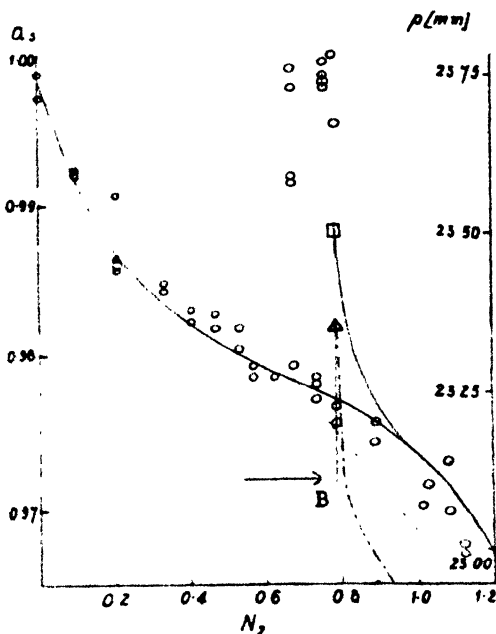


FIG. 2.

¹⁰ *J. Amer. Chem. Soc.*, 1921, 43, 102.

¹¹ *Trans. Chem. Soc.*, 1932, 553.

for pure KCl solutions at a distance corresponding to Δp circa 0.04 mm. until near 1.3 $M.$, then to rise rapidly to a maximum value of Δp circa 0.15 mm., then to approach the KCl curve and to cut it at about 0.7 $M.$, passing beneath it and away to a maximum distance corresponding to about 0.15 mm., and finally to approach it again, finishing below it at a value corresponding to the vapour pressure curve of a saturated aqueous solution of PbCl_2 .

The calculated curve, on the other hand, runs below the curve for the pure KCl solution, its distance steadily increasing from about 2 $M.$ downwards, until, at about 1 $M.$, it reaches a maximum value where Δp is 0.15 mm.; after which it rises more rapidly, finally shooting upwards, crossing the KCl curve at 0.81 $M.$ and ending at 0.791 $M.$ (point marked by triangle) with a value of $a_3 = 0.9822$. Until 0.8 $M.$, where the experimental and calculated curves cross, the former is above the latter, and by distances corresponding to values of Δp which are throughout much greater than the experimental error—thus, by about 0.1 mm. at 1.8 $M.$ and perhaps by 0.25–0.3 mm. between 1 to 1.2 $M.$ KCl, a region which corresponds to a concentration range on the equilibrium diagram over which $[\text{PbCl}_2]$ is changing very slowly with change of $[\text{KCl}]$.¹²

We do not think that the data recorded in this paper can be seriously questioned; the reason for the discrepancy must lie in the E.M.F. figures from which the calculated curve was obtained, or in the graphical integration by means of which these data were worked up, using the expression

$$\int d \log a_3 = \int \frac{2N_2 - N_1}{N_3} \cdot d \log a_1$$

If we consider this integration between the invariant point C and a concentration just over 0.8 $M.$, the point at which the experimental and calculated curves cross, then experimental and calculated values of $\Delta \log a_3$ become identical, *i.e.* the area obtained by plotting $f(N)$ or $(2N_2 - N_1)/N_3$ against $\log a_1$ over this concentration range is numerically correct, and the discrepancies under discussion are to be ascribed to incorrect correlation between the $f(N)$ and the $\log a_1$ values when plotting these against one another. This, in its turn, may be due either to incorrect or to insufficient E.M.F. data, the latter because interpolation of experimental values is necessary when drawing the graph of $\text{E.M.F.}/N_2$ before carrying out the graphical integration. Inspection of Table II., Part II., shows that only five experimental values of E.M.F. were available between point C and $N_2 = 1$, whilst, between this concentration and 0.8 $M.$, the experimental data were so discordant that recourse had to be made to extrapolation devices when estimating the figures finally used (Table III., *loc. cit.* 2).

Assuming our experimental results to be represented by the full line in Figs. 1 and 2, we have accordingly applied to them the above equation in the form

$$\Delta \log a_3 = \left(\frac{2N_2 - N_1}{N_3} \right)_{\text{mean}} \Delta \log a_1$$

The experimental curve was divided into a number of sections, each with its definite terminal figures for a_3 , N_1 and N_2 (N_3 is always 55.5). The terminal values of $(2N_2 - N_1)/N_3$ were calculated from the known

¹² See reference 2, Fig. 1.

composition of the liquid phase, and the mean value taken. This was divided into $\Delta \log a_3$ obtained from the experimental data, and $\Delta \log a_1$, i.e. the increment in $\log a_1$ when passing from one end of the concentration section to the other, thus calculated. When $f(N)$ was plotted against $\log a_1$, the result was a strip of area equal to $\Delta \log a_3$. Commencing at the invariant point C ($N_2 = 3.096$; $f(N) = 0.1142$), where $\log a_1$ is $\bar{1}.2796$, this procedure was followed down to $N_2 = 0.9$, the concentration range being divided into seventeen sections, a method which reduced to a minimum any inaccuracy involved in assuming $f(N)$ to be a linear function of $\log a_1$ inside any particular section.

The plane figure obtained was practically identical down to $2.25 M.$ with that constructed when working up the E.M.F. data in Part II., in accordance with the fact that, over this concentration range, the experimental and calculated curves for a_3 run close to and parallel to one another (Fig. 1). Below this point, the area of the new figure became progressively greater than that of the former one, corresponding to the increasing divergence between the experimental and calculated curves for a_3 . At $N_2 = 0.9$ ($f(N) = 0.0326$), $\log a_1$ was $\bar{1}.8043$, whereas the electrometric data, on which the former graphical integration was based, had given $\bar{1}.762$. When, using the expression

$$\log a_1 = (0.4837 - E)/0.02957,$$

the values of E were calculated systematically over the whole concentration range from the new diagram, it became plain that insufficiency of E.M.F. data was not responsible for the divergence between the experimental and calculated values of a_3 . Down to $2 M.$, the calculated values of E fell on the old experimental E/N_2 curve. But at lower concentrations they were below those actually determined, the discrepancy being about 0.0005 volt at $1.5 M.$, rapidly increasing below $1.3 M.$, reaching a maximum of > 0.002 volt at $1.05 - 1.1 M.$ (concentration of maximum difference between experimental and calculated a_3 values), and then diminishing. The values of a_1 electrometrically determined, as in the case just quoted, are lower than those calculated from vapour pressure measurements. Attention has already been drawn to the discussion in Part II of the discordant results obtained when experimenting in this concentration region, both when attempting to determine the exact shape of the equilibrium diagram and in the measurement of E.M.F. In the latter case, solutions presumed to be of the same composition made up at different times gave E.M.F.s differing by amounts up to 0.0003 volt. Returning to the $f(N)/\log a_1$ diagram under discussion, a further point of considerable interest arises. In order to complete it, it must be carried to the non-variant point B, where PbCl_2 is one of the solid phases and $\log a_1$ consequently 0.0 . This non-variant point has been approximately (see Part II.) fixed at concentrations of KCl and PbCl_2 which give a value of $f(N) = 0.0283$, a figure which will not be seriously affected by the uncertainty regarding the exact position of B. Taking these facts into account, the increment in $\log a_3$ when passing from $N_2 = 0.9$, where $\log a_1$ is $\bar{1}.8043$, to B *cannot be less than* 0.0283 ($0.0 - \bar{1}.8043$), i.e. 0.00554 and will probably be greater. At $N_2 = 0.9$, a_3 (experimental) is 0.975 and $\log a_3$ 0.9890 . It follows that, at B, $\log a_3$ will be *at least* 0.9945 and a_3 *at least* 0.9874 . The $f(N)/\log a_1$ diagram when completed graphically gives 0.0400 as the most probable value for $\Delta \log a_3$ when passing from C to B. At C, $\log a_3$ is $\bar{1}.9549$; hence it is $\bar{1}.9949$ at B and

a_3 is 0.9883. The experimental curve for a_3 in Figs. 1 and 2 has been extrapolated in this way to point B (denoted by square on diagrams). Like the curve calculated from the E.M.F. data, it bends up very sharply at the end; but it must be realised that its construction in the present case does not involve any E.M.F. data other than the figures corresponding to the two non-variant points bounding the solubility curve of 2PbCl_2 , KCl. About the essential correctness of these, there can be no reasonable doubt.

The value of 0.9883 for a_3 at B, obtained from these two E.M.F. measurements and our own vapour pressure data, lies then far above the two direct determinations (0.9767 and 0.9756—see Expts. 53 and 54, Table II.), which it would be natural to regard as normal, whilst falling below the third, abnormal value (0.9954—Expt. 52). It furnishes an independent reason for considering that the abnormal figures in general (italicised in Table II.) found between this value of N_2 and 0.678 are not merely due to some unusual experimental error. Similar high vapour pressures recorded for unsaturated solutions in the same KCl concentration region are italicised in Table I. We ourselves, whilst being unable to explain their spasmodic appearance, do not doubt that they represent the actual vapour pressures exerted by the systems in question under the experimental conditions. They were never observed except with solutions of N_2 values between 0.678–0.804 (50–60 grams/litre KCl). Four out of seven experiments with unsaturated solutions in this concentration range gave abnormally high vapour pressure values, and ten out of sixteen experiments with saturated solutions. The results of the sequence of Expts. 55–74 is of interest. Expts. 55–65 were on solutions between 1.65 *M*. and saturation and gave normal results; in Expt. 66, N_2 was 0.782 and the vapour pressure exceptionally high; Expts. 67–70 (KCl 1.032 *M*. and saturated) gave normal results, whilst in 71–72, N_2 lay in the critical range and the results were high; in Expt. 73, N_2 was 0.536 and the vapour pressure normal, whilst Expt. 74 ($N_2 = 0.804$) gave a very high figure.

One of the abnormal values (Expt. 78, Table I.) was given by a solution containing KCl only, its vapour pressure being almost 1 per cent. above the generally recognised figure. Unpublished measurements of Dr. L. Nickels have shown that the minimum of the viscosity-molality curve for KCl solutions at 25°C . lies at about 0.75 *M*., and the view that a "negative" viscosity is due to the depolymerising effects of the solute on the molecules of the solvent is well known. Monohydrol would, of course, have a very high vapour pressure at 25° , and it would only need a slight displacement of the normal equilibrium between it and its polymers to cause a considerable rise in the vapour pressure of water. These facts suggested that an intensive investigation of the vapour pressures of pure KCl solutions in this concentration region might give results of interest. Such work has been done, using a variety of experimental methods. Some very curious and some quite normal results have been obtained, and it is hoped shortly to publish them.

Omitting consideration of the abnormal region, the general course of our experimental curve furnishes evidence of the presence of complexes in solution, in agreement with their isolation in the solid state. At low KCl concentrations, the effects of the dissolved KCl and PbCl_2 on the vapour pressure of the solvent tend to be additive. As $[\text{KCl}]$ increases, complex formation becomes so important that the vapour pressures of the solutions actually exceed those of solutions of pure KCl of the same

KCl molality. Further increase in $\{KCl\}$ causes this effect to become relatively less important, and the curves approach one another again. The observations made in the region of the abnormal vapour pressures, as also the sudden changes in slope of the experimental curve between 1 and 1.3 *M.* show, however, that this simple conception is insufficient to explain completely the nature of the system.

Thermodynamic treatment of the experimental curve at KCl concentrations below B is impossible owing to the ill-defined values of a_3 in the critical concentration range.

Summary.

(1) The measurement at 25° C. of the aqueous vapour pressures of solutions containing KCl and PbCl₂ in equilibrium with various solid phases, as also of certain unsaturated solutions is described.

(2) The results are not in agreement with previous calculations made from electrometric work carried out on the same system. An examination of the discrepancies leads to the conclusion that the electrometric data are of insufficient accuracy.

(3) Over a narrow concentration region, abnormally high aqueous vapour pressures, approaching that of pure water, were frequently observed. This region is the same one in which discordant analytical and E.M.F. data had previously been obtained.

These experiments were carried out during the sessions 1927-29. One of us (E. H.) wishes to acknowledge his indebtedness to the Department of Scientific and Industrial Research for a maintenance grant received by him over this period.

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THE ABSORPTION SPECTRUM OF SULPHUR TRIOXIDE.

BY E. FAJANS AND C. F. GOODEVE.

Received 17th December, 1935.

No measurements of the absorption spectrum of pure SO₃ have been recorded. Dutt¹ studied the absorption of SO₂-SO₃ mixtures and claimed to be able to eliminate the effect of the former. "Continuous absorption" from 3300 to 2600 Å and from 2300 Å downwards was found and attributed to SO₃. The present investigation in which the SO₂ content is reduced to a very low value, has not confirmed these conclusions.

Experimental.

The absorption spectrum of SO₃ was examined by means of a small Hilger quartz spectrograph, E. 370, and later by a medium Hilger quartz, E. 3. Wave-lengths were determined by comparison with a copper arc. A hydrogen discharge tube was used as a source of continuous ultra-violet

¹ A. K. Dutt, *Proc. Roy. Soc.*, 1932, **137A**, 366.

light. Absorption tubes of 54 cm. and 346 cm. lengths were used. Joints between quartz and glass were sealed with sodium silicate and aged by leaving in contact with gaseous SO_2 for some days. As SO_2 attacks mercury even when dry, pressures were measured by means of a calibrated quartz Bodenstein gauge.*

The SO_2 was prepared by distilling *in vacuo* pure fuming sulphuric acid and fractionating between traps cooled in liquid air. The first and last fractions were rejected by sealing off the requisite traps. Removal

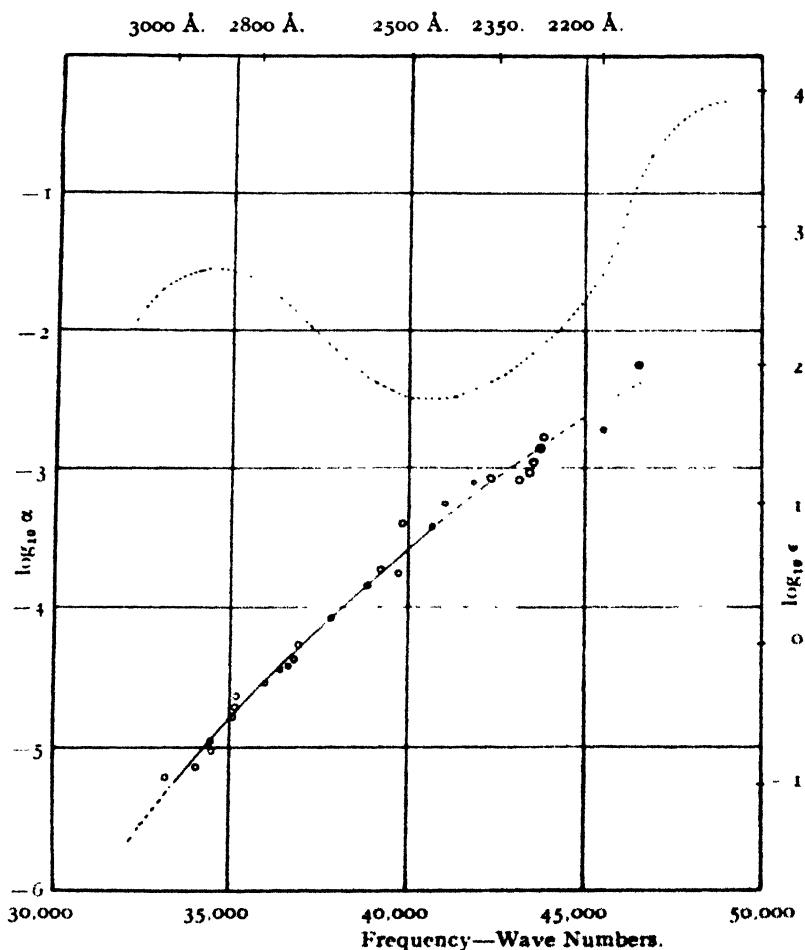


FIG. 1.—The absorption curve of sulphur trioxide (full line) and of sulphur dioxide (dotted line—approximate curve).

of the dioxide by fractionation is insufficient as it is reproduced rapidly during a measurement by photodecomposition of the SO_2 . Complete elimination of the absorption bands of SO_2 down to 2200 Å. was obtained by streaming the purified gas rapidly through the absorption tubes between traps at the ends.

The first photographic exposure was taken with liquid air on the traps and the intensity of the light reduced a definite amount by means of a rotating sector. The liquid air was then removed and the desired pressure

* J. W. Goodeve, *Trans. Faraday Soc.*, 1934, 30, 501.

and velocity of flow of SO_2 obtained by careful regulation of the temperatures of the end traps. With the sector open a second exposure through the gas was taken in an adjacent position on the photographic plate. A third adjacent spectrum was taken identical to the first, to test the constancy of the light source. The extinction coefficient α was obtained for the wave-length of the "match point," by the equation

$$\alpha = \frac{1}{p \cdot l} \cdot \log_{10} \frac{I_0}{I_r} = \frac{1}{p \cdot l} \cdot \log S,$$

where p is the pressure in mm. of Hg, l the length of the tube in cm., and S the sector angle. The molecular extinction ϵ was calculated by the equation,

$$\epsilon = \frac{1}{c \cdot l} \cdot \log_{10} S,$$

where c is the concentration in gram molecules per litre, calculated assuming the temperature to be 18°C . Pressures in the range of 1 to 160 mm. were obtained and could be kept constant to within 5 per cent., except below 10 mm.

Results.

The absorption spectrum of sulphur trioxide was observed between 3000 and 2200 Å and found to consist of weak diffuse bands superimposed on a continuous background. The logarithms of the extinction coefficients

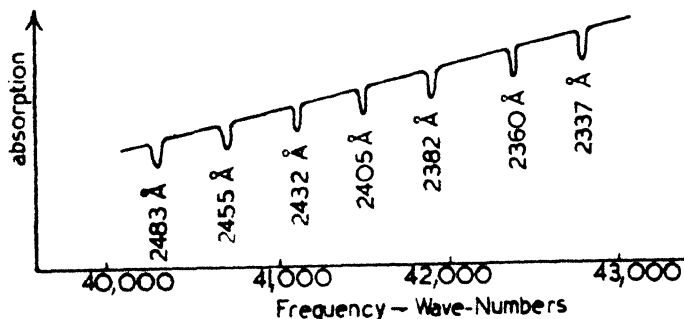


FIG. 2.—The absorption in the region of the diffuse bands.

obtained as described above are shown in Fig. 1, plotted against frequency. It was found impossible to obtain reliable measurements below 2200 Å. owing to the very strong SO_2 absorption in this region.

The observed diffuse bands were of an unusual type. The maxima of absorption were flat and the minima sharp as indicated diagrammatically in Fig. 2. The distance between the minima was found to be approximately constant and equal to 430 W.N. It may be possible at some time to correlate this with a fundamental frequency of the molecule. The diffuse bands appear to extend to about 2700 Å., but above 2500 Å. they could not be measured with certainty. These bands cannot be attributed to SO_2 , as they occur at the position of minimum absorption of the latter. It is unlikely that they are due to other impurities as they always appeared with the same intensity under the same conditions. They are probably predissociation bands.

Discussion.

The observations recorded here indicate that the absorption of SO_2 is of a different character and in a different position from that found

by Dutt. He claims that "it is possible to eliminate the SO_2 bands from the plate by putting an excess of oxygen in the absorption chamber and then filling it up with SO_2 vapour. According to the law of mass action the partial pressure of SO_2 is very considerably reduced by the addition of O_2 ." It is well known that even in the presence of a catalyst SO_2 does not react with oxygen at room temperature.

Approximate values of the extinction coefficients of SO_2 have been calculated from the results of Garret³ and from a photometric curve of Kornfeld and Weegmann.⁴ These are indicated by the broken line in Fig. 1. It is seen that at some wave-lengths one part in one thousand of SO_2 is sufficient completely to mask the absorption of SO_2 . The coincidence between the limits of absorption found by Dutt and those for SO_2 , coupled with the above argument, leads to the conclusion that his observations were due to the presence of the dioxide.

The decomposition of SO_2 into SO and normal O atoms requires 81.3 K cal. (Landolt-Börnstein). This corresponds to a wave-length of 3500 Å. It is probable that this is the primary photochemical process in most of the ultra-violet range. Coehn and Becker⁵ found that SO_2 decomposes photochemically by light transmitted through "Uviol-glass" (transparent⁶ to about 2500 Å). At wave-lengths below 2500 Å. it is possible for excited D oxygen atoms to be produced.

Our thanks are due to Professor Donnan for his interest and encouragement in this work.

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³ C. S. Garret, *Phil. Mag.*, 1916, **31**, 505.

⁴ Kornfeld and Weegmann, *Z. Elektrochemie*, 1930, **36**, 789.

⁵ Coehn and Becker, *Z. Elektr.*, 1907, **13**, 545; *Z. physik. Chem.*, 1910, **70**, 88.

⁶ Weigert, *Opt. Methoden d. Chemie*, p. 54.

THE PHOTOCHEMICAL FORMATION OF ORGANIC DIRADICALS. PART III.* INVESTIGATIONS ON ANTHRACENE, THE FULGIDES, THIO-PHOSGENE AND THEIR DERIVATIVES.

BY ALEXANDER SCHÖNBERG.

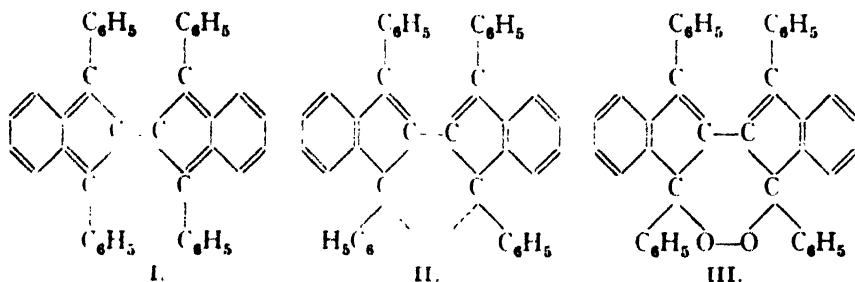
Received 29th November, 1935.

1. In a previous communication,¹ I showed that the remarkable behaviour of rubrene towards oxygen in light is accounted for in the following way. Rubrene in the dark has the formula I, in agreement with the fact that either in solution or in the solid state, it is stable to air provided it is kept in the dark. If the solution, however, is irradiated a photoequilibrium occurs between the normal form and the diradical

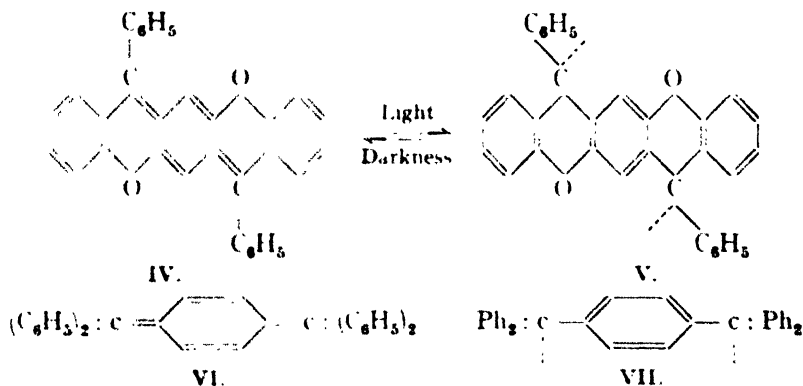
* *Annalen*, 1935, **518**, 299; *Ber.*, 1934, **67**, 633.

¹ *Ibid.*, 1934, **67**, 633.

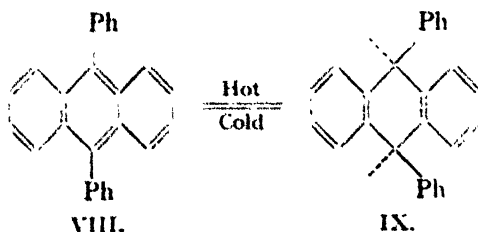
form (II). The latter, containing as it does two trivalent carbon atoms, can form a peroxide (III), by the addition of oxygen.



Recently I pointed out further ² that chromanorufen (IV) and tetraphenyl-*p*-quinodimethane (VI) are to be regarded as the analogues of rubrene. Their solutions in the absence of light are extremely stable to oxygen, but in light they quickly lose their colour, as in irradiated solutions a photoequilibrium is set up between the normal and diradical forms (V and VII). The latter, on account of their trivalent carbon atoms, can react with oxygen.



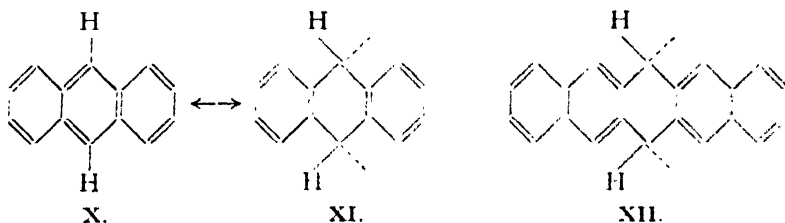
2. It will now be shown that similar considerations can be applied to anthracene and its derivatives. The assumption that anthracene and its derivatives can exist as diradicals has been made repeatedly. For example, Ingold and Marshall ³ showed that a solution of 9-10-diphenylanthracene (VIII) changes its colour on warming and explained this fact by assuming that heating shifts the equilibrium between the normal form (VIII) and the diradical form (IX) in favour of the latter.



² *Annalen*, 1935, 518, 300.

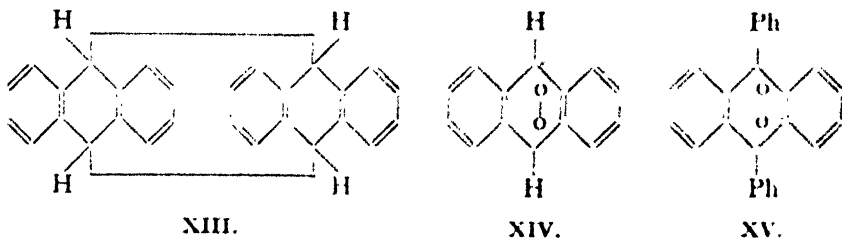
³ *J. Chem. Soc.*, 1926, 3080.

Dufraisse and Étienne⁴ also recognised that 9-10-diphenylanthracene is capable of forming an equilibrium mixture $\text{VIII} \rightleftharpoons \text{IX}$. Clar⁵ states that the characteristic properties of anthracene derivatives can best be accounted for by equilibrium formulæ of the type represented by $\text{X} \rightleftharpoons \text{XI}$. In the case of one derivative, 2-3-6-7-dibenzanthracene, a deep coloured compound, he assumes that it exists *only*⁶ in the diyl-form XII.



All such considerations deal with the occurrence of diradicals in *thermo*-equilibrium with the normal molecules. This assumption, however, is not in accordance with the following facts. No peroxide formation in the dark has been observed in the case of anthracene, 9-10-diphenylanthracene, and 2-3-6-7-dibenzanthracene. Further, magnetic measurements on 2-3-6-7-dibenzanthracene, contrary to Clar's assumption, have shown that this compound does not exist entirely in the diradical form. If in thermoequilibrium its molecules exist in the diradical form, their concentration is so small that they cannot be detected by magnetic measurements.⁷ Summarising, it can be said that on the whole there is little experimental evidence for the existence of a *thermo*equilibrium of diradicals in the field of anthracene, though the work of Ingold⁸ shows that in certain cases such equilibria probably occur.

I believe, however, that in irradiated solutions of the above compounds a *photo*equilibrium exists between the normal and the diradical forms. On this assumption it is easy to explain why *irradiated* solutions of anthracene, 9-10-diphenylanthracene, and 2-3-6-7-dibenzanthracene react with oxygen. It is simply a question of the action of oxygen on the trivalent carbon atoms of the *photodiradicals* IX, XI, and XII. The formation and structure of the oxidation products of anthracene and 9-10-diphenylanthracene have been definitely established by the investigations of Dufraisse and Gérard,⁸ and Dufraisse and Étienne.⁹ They possess the formulæ XIV and XV respectively. The structure of the compound formed by the action of oxygen on 2-3-6-7-dibenzanthracene is unknown.



⁴ *Comptes rendus*, 1935, **201**, 280.

⁵ *Ibid.*, 1930, **63**, 2967.

⁷ Müller and Müller-Rodloff, *Annalen*, 1935, **517**, 146.

⁸ *Comptes rendus*, 1935, **201**, 428.

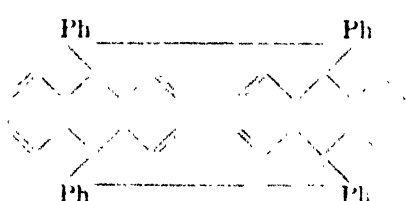
⁵ *Ber.*, 1932, **65**, 503.

⁹ *Ibid.*, 280.

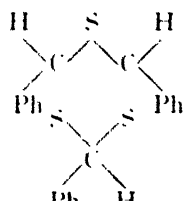
The photopolymerisation of anthracene to dianthracene (XIII) is also most readily explained by the assumption that the diradical XI is an intermediate. It is not proposed to discuss in this paper whether XIII is formed by the direct combination of two diradicals or by means of a more complicated process.^{10, 10a}

The objection might be raised that a photodimerisation of 9-10-diphenylanthracene has not yet been observed, and this used as an argument against the theory of biradical formation in irradiated solutions of 9-10-diphenylanthracene (IX). The non-occurrence of the dimeric 9-10-diphenylanthracene XVI, however, is probably due to its thermolability and, in my opinion, does not contradict the theory outlined above. From our knowledge of the relationship between constitution and stability to heat, the compound XVI must be thermolabile, and, indeed, considerably more labile than the rather thermolabile dianthracene which decomposes above 150° into two anthracene molecules.¹¹

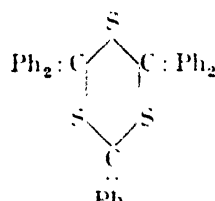
It may be for this reason that the presence of XVI could not be detected, possibly the compound at room temperature being incapable of existence or of existing for only a limited time. To avoid a lengthy discussion, I will content myself by pointing out the following analogies: Dianthracene (XIII) is related to the compound XVI as 1-1-2-2-tetraphenylethane (relatively thermo-stable) to hexaphenylethane (thermolabile); as 1-2-diphenylhydrazine (relatively thermo-stable) to tetraphenylhydrazine (thermolabile); or as trithiobenzaldehyde (XVII) (thermo-stable) to trithiobenzophenone (XVIII). This last compound is so thermolabile that no method for synthesising it has yet been found.



XVI.

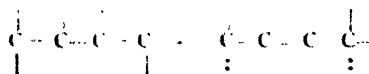


XVII.

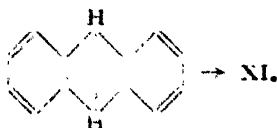


XVIII.

¹⁰ Cf. Weigert and Jackh, *Naturwissenschaften*, 1927, 15, 124. The above ideas of the photochemical transformation of a system of conjugated double bonds to a biradical system



have nothing in common with the considerations of other authors who assume that in irradiated solutions of anthracene the following process takes place, involving the rupture of an ethane linkage. (Cf. Weigert, *Naturwiss.*, 15, 124; Weigert and Pruckner, *Z. physik. Chemie, Bodenstein Festband*, 1931, 775).



^{10a} Formula XI. contains trivalent carbon atoms, one of the valences of each of these atoms being saturated with hydrogen. Such an assumption finds support in the existence of a similarly built monoradical formed by a reaction in the dark. (Cf. Wittig and B. Obermann, *Ber.*, 1935, 68, 2214) (added in proof).

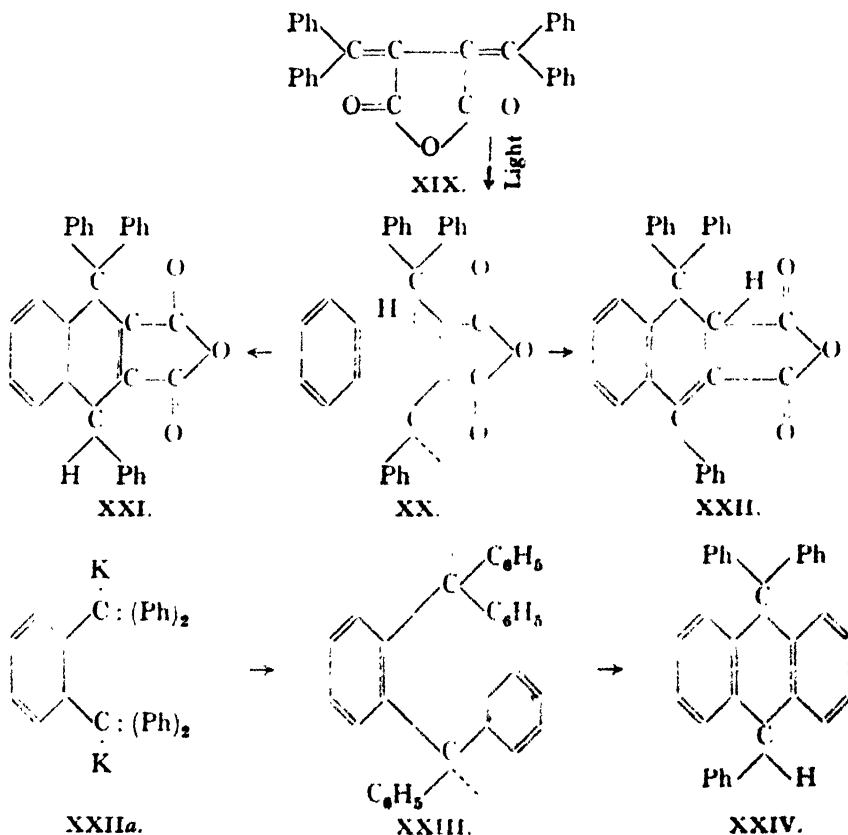
¹¹ W. Jackh, *Dissertation, Leipzig*, 1927, p. 21.

Reactions which might be expected to form it, yield instead its dissociation product thiobenzophenone.¹²

3. The fulgides possess certain properties which have been difficult to understand, but which can be readily explained by the diradical theory as the following example shows. Tetraphenyl-fulgide (XIX) is changed by *light* into the two isomers XXI and XXII.¹³

This reaction is difficult to understand if one starts from formula XIX for tetraphenylfulgide. Assuming, however, that it is a question of a reaction of the diradical XX, then the reaction can be simply explained. There are many analogies to this mechanism in the field of free radicals. For example,¹⁴ the formation of XXIV from XXIII in the course of a dark reaction.

W. Schlenk and E. Bergmann¹⁵ have assumed that the molecules of certain fulgides are in *thermo*equilibrium with diradicals and that the concentration of the latter increases with rise in temperature. In this way they have tried to explain the reversible alterations in colour which certain fulgides undergo on warming.



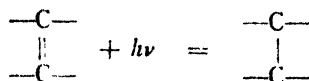
¹² Cf. Schönberg, *Ber.*, 1929, **62**, 195.

¹³ Observation by H. Stobbe. Described by J. Houben in his *Methoden der organischen Chemie*, Vol. II., p. 1033. Leipzig, 1922.

¹⁴ Wittig and Leo, *Ber.*, 1931, **64**, 2369; Müller and Müller-Rodloff, *Annalen*, 1935, **517**, 148.

¹⁵ *Ausführliches Lehrbuch der organischen Chemie*, Vol. I., p. 520.

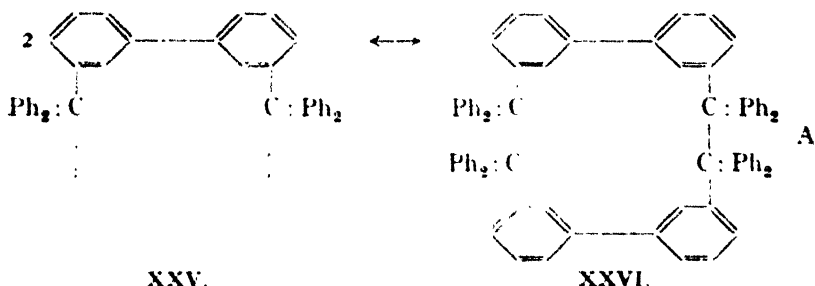
4. The photochemical change of maleic and fumaric acids into one another has been explained by the assumption that both acids possess the same excited electron state (*Elektronenzustand*) with a single carbon to carbon linkage brought about by absorption by molecules of either acid. Olsen¹⁶ formulates the process as follows:



There exists, from the standpoint of the biradical theory, great similarity between maleic and fumaric acids on the one hand and the compounds I, IV, VI, and VIII on the other, since the last four compounds can also be converted by light into diradicals. Whether or not this similarity is quantitative will not be fully discussed here. If the analogy holds quantitatively, then for example in the case of diphenylanthracene the equation $\text{VIII} + h\nu = \text{IX}$ must hold, but the formation of the diradical IX may be more complicated, e.g.

$\text{VIII} + h\nu = \text{diphenylanthracene}^*$. Diphenylanthracene* means that the molecule is in an excited condition which differs from IX, and that IX results from diphenylanthracene* by secondary reactions in the dark, possibly through collision with one or more molecules of VIII or of the solvent. Similar modes of formation of the other diradicals which have been discussed in this paper can be postulated.

5. The capacity of diradicals to exist in equilibrium in the dark has long been known.¹⁷ In the case A, the accepted view has recently been



confirmed by magneto-chemical measurements.¹⁸ It will be very difficult to prove the existence of diradicals in irradiated solutions of I, IV, VI, VIII, X, and XIX by magnetic measurements. The equilibrium point between the normal and the corresponding diradical depends among other things on the intensity of the effective frequency of the light used. Where the life-period of the photo-diradical is short, it will be difficult to obtain photo-systems in which the concentration of the diradical form is reasonably great in comparison with the concentration of the normal form. Such conditions, however, are necessary for the detection of diradicals by magnetic measurements (*cf.* the lack of sensitivity of the known experimental methods).

Eugen Müller¹⁹ states that radiated solutions of rubrene cannot be

¹⁶ *Trans. Faraday Soc.*, 1931, **27**, 69. Compare also K. F. Bonhoeffer and P. Hartack, *Grundlagen der Photochemie*, Dresden and Leipzig, 1933, p. 269.

¹⁷ *Cf.* Schlenk and Brauns, *Ber.*, 1915, **48**, 716.

¹⁸ Müller and Müller-Rodloff, *Annalen*, 1935, **517**, 144.

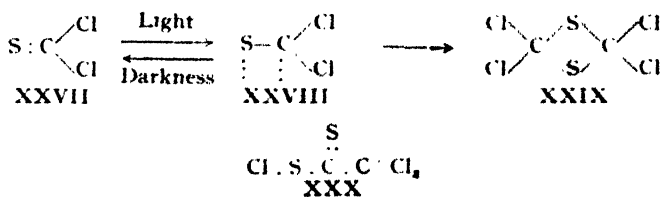
¹⁹ *Z. Elektrochem.*, 1934, **40**, 542.

distinguished from non-irradiated solutions by magnetic measurements. His results have been used as an argument against the diradical theory.²⁰ This, however, is not applicable for the reasons given above. In addition in Müller's paper no details whatever are given about the optical conditions used. (Intensity of the radiation frequency, conditions of absorption.) Müller himself seems to hold that his experimental results do not contradict the diradical theory.²¹

It might be asked why, in irradiated solutions of rubrene, there is considerable chemical reactivity of the diradicals although their concentration in photo-chemical equilibrium is very small. It should be pointed out that for the *chemical* properties of the photo system $I \rightleftharpoons II$ the decisive factor is not the relative concentration of II but the quickness with which II is regenerated when the photo-equilibrium $I \rightleftharpoons II$ is disturbed by chemical reactions. This is the reason why irradiated solutions of rubrene react quickly with oxygen even when the relative concentration of the biradical form is very small. All that has been stated above about rubrene solutions can be applied to other photosystems.

6. It must on no account be assumed that the photo-chemical formation of diradicals is limited to the formation of two trivalent carbon atoms within one molecule. A case in point is that of thiophosgene (XXVII). Recently, with Stephenson,²² I showed that the photodimerisation of thiophosgene does not yield the compound XXX as had previously been assumed, but that the photodimer had the structure XXIX.^{22a} The process is analogous to that of the dimerisation of anthracene, and it can be assumed in this case also that in the irradiated solutions of thiophosgene a *photo-chemical* equilibrium exists ($XXVII \rightleftharpoons XXVIII$). Evidence for the analogy is further found in the properties of the dimers XIII and XXIX which depolymerise on heating.

The quantum sensitivity of the photo-chemical polymerisation of anthracene has been frequently investigated.²³ It might perhaps be desirable to test the above views and hypotheses of the polymerisation of anthracene in the system $XXVII \rightarrow XXIX$, but circumstances do not permit me to do so. Since thiophosgene is red and the photodimer XXIX colourless, it would be easy to estimate colorimetrically the concentration of thiophosgene in any given system. Consequently, the quantum yield should be easily determined.



Unfortunately, the number of organic photo-chemical reactions which have been investigated with regard to their quantum sensitivity is small, since only a few reactions are suitable for such investigations. I might mention in this connection the photodecomposition of the colourless ion

²⁰ Cf. Richter-Anschütz, *Chemie der Kohlenstoff Verbindungen*, 12th edition, Vol. II., part 2, p. 651, 1935.

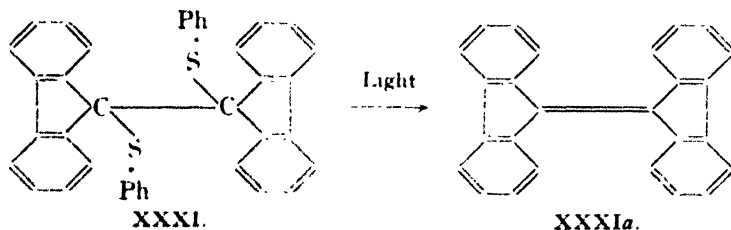
²¹ *Annalen*, 1935, 517, 146.

²² *Ber.*, 1933, 66, 567.

^{22a} This formula has just been confirmed by Delépine and co-workers, *Bull. Soc. Chim.*, 1938, 1969 (added in proof).

²³ Luther and Weigert, *Z. physik. Chemie*, 1905, 51, 297; 1905, 53, 385; Weigert, *Ber.*, 1909, 42, 850; Weigert and Jackh, *Naturwissenschaften*, 1927, 15, 124; Byk, *Z. physik. Chemie*, 1908, 62, 454.

$\alpha\beta$ -diphenylthiol - $\alpha\beta$ -di (diphenylene-ethane) XXXI.²⁴ The decomposition product XXXIa is red, so that it is easy in this case also to estimate the quantity of decomposition product colorimetrically and from this the quantum sensitivity.



The author thanks Dr. Neil Campbell for his assistance in the translation of the manuscript, and acknowledges his profound gratitude to Professor G. Barger for his hospitality.

Summary.

1. The author shows that from his earlier work on irradiated solutions of rubrene a photoequilibrium ($I \rightleftharpoons II$) between the normal and diradical form is set up. In order to explain the different chemical properties of irradiated solution of certain anthracenes, fulgides, and thiophosgene in comparison with those of non-irradiated solutions, he assumes that an analogous photoequilibrium occurs. The phenomena of photo-oxidation, photoisomerisation, and photopolymerisation in such solutions are thus explained.

2. The difficulty or impossibility of establishing the presence of diradicals in these photoequilibria by magneto-chemical measurements is discussed.

3. It is shown, from the structure of the photodimer of thiophosgene previously advanced by the author, that the photopolymerisation of thiophosgene is an analogous process to that of the photopolymerisation of anthracene. The consequences arising from this are discussed.

4. By considering the relationship between constitution and stability to heat of organic compounds, it is explained why the dimers of certain photodiradicals are incapable of existence.

University of Edinburgh
(*Medical Chemistry Department*).

²⁴ Schönberg and Stolpp, *Annalen*, 1930, 483, 102.

REVIEWS OF BOOKS.

The Teaching of Chemistry in the Universities of Aberdeen (Aberdeen University Studies No. 112). By ALEXANDER FINDLAY (Aberdeen: The University Press, 1935. Pp. viii + 92).

Professor Findlay has traced the history of the teaching of Chemistry in Aberdeen from the earliest period until 1914. A Chair of Chemistry was founded in 1793, although private lectures on the subject had been given in 1783. One of the professors was Thomas Clark (1833-1860), who discovered metaphosphoric acid and invented the water-softening process. Other well-known names are Carnelley and Japp: the account closes with

the retirement of the latter. Professor Findlay has dealt with his materia in a very skilful way, and the result is a work of scholarship which is at the same time full of interest on the personal side.

J. R. P.

Principles and Applications of Electrochemistry. Vol. I. Principles.

By H. JERMAIN CREIGHTON. John Wiley & Sons., Inc., New York; Chapman & Hall, Ltd., London. Third edition, 1935. Pp. 502. Price 20s.

The continued demand for Professor Creighton's well-known book has necessitated the publication of a third edition, and the author has taken the opportunity to re-write certain portions and to add some new matter. In addition to the topics generally included in the subject of electrochemistry the book contains short chapters on electrokinetic phenomena and on the electrochemistry of gases; fused electrolytes are also mentioned from time to time. The material added in the present edition deals chiefly with the measurement of conductivity and application of the results for the purpose of testing the Onsager equation, with the determination of transport numbers by the moving-boundary method, with potentiometric titration, and with the glass electrode. A number of new references are also to be found in other sections of the book. It is perhaps surprising that the chapter on the relationship between chemical structure and the dissociation constants of acids and bases is unaltered from the first edition: as this subject has moved so definitely into the province of organic chemistry in recent years the author might find it advisable in a later edition to leave this short portion out of the book entirely. The highly speculative, if picturesque, method for the calculation of ionic hydration proposed by Remy could also be omitted without serious loss. The section on the activity of strong electrolytes is short but quite adequate for the purpose of the book; in it the author says "the concept of activity has been used very extensively in the recent study of strong electrolytes, and its utility has been fully justified." Nevertheless it is a matter for regret that apart from the chapter mentioned and the following one on theories of strong electrolytes, the activity idea is not used, not even in the discussion of E.M.F. Apart from this omission, which may have been made intentionally to simplify the treatment, the book forms a useful introduction to many aspects of electrochemistry, and its excellent production and clear printing should make an appeal to students of the subject.

S. G.

The Chemistry of Rubber. By H. FREUNDLICH. London: Methuen, 1935. Pp. xi + 72. Price, 2s. 6d. net.

This short essay deals with the colloid chemistry of latex and raw rubber, together with a few remarks on vulcanisation and plantation history, so that the title is somewhat misleading. The treatment is too compressed to make any part of the book adequate, but it serves as an interesting summary of the outstanding colloid problems of the industry. A stimulating feature is the number of difficult questions stated and left as unanswerable in the present state of knowledge.

T. R. D. and B. D. P.

Étude Thermodynamique de la Tension Superficielle. By RAYMOND DEFAY. Paris: Gauthier-Villars & Cie, 1934. 372 pp.

Although the two monographs forming this book deal with related subjects, either can be read independently of the other. They will be reviewed separately.

Part I. Formules générales. Affinité et vitesse d'adsorption. Catalyse. Équilibre. Influence de la courbure.

Gibbs' classical work on "The equilibrium of chemical substances" deals almost entirely with the thermodynamic conditions governing systems in complete equilibrium, but Gibbs' methods are easily extended to deal with systems only in partial equilibrium. In Defay's first monograph he applies these methods to chemical systems in which there is thermal and mechanical equilibrium throughout the system and chemical equilibrium in each phase, but not necessarily equilibrium between the surfaces and the bulk phases. Defay derives over 500 equations for these systems. They appear to be correct without exception, but the majority of them are neither very interesting nor very useful. Most of them answer questions of the type: how does the surface tension depend on the temperature (or on the pressure) when the compositions of all bulk phases and all surfaces are kept unchanged, a condition practically impossible to fulfil? Yet the most obviously useful questions are ignored, such as: how does the surface tension depend on the temperature (or on the pressure) when equilibrium is maintained throughout the system? Many of the formulæ are effectively mere repetitions of others depending, for instance, on a change from mole fractions to mole ratios.

Defay follows De Donder in replacing Gibbs' conception of the "number of independent components" by the total number of chemical species diminished by the number of distinct chemical reactions between them. This seems to complicate the formulæ without any compensating advantage. It is admittedly difficult to define clearly and simply the number of "independent components," but no more so than the number of "distinct" chemical reactions. The author conscientiously gives a mathematical definition of this number, which is far from simple, but it is placed anomalously in the second monograph.

The author goes to much pains to show that the position of the geometrical dividing surface is not arbitrary. He appears to have overlooked Gibbs' clear pronouncement on this point. "The value of σ is therefore independent of the position of the dividing surface when this surface is plane. But when we call this quantity the superficial tension, we must remember that it will not have its characteristic properties as a tension with reference to any surface. Considered as a tension its position is in the surface which we have called the surface of tension and nowhere else." (*Collected Works*, p. 234.)

This work, in common with other work by De Donder and his school, is, in the reviewer's opinion, marred by the attempt to apply thermodynamics to chemical kinetics. All progress in this field has come from considerations of molecular mechanism, and the idea that a reaction rate is determined by the affinity of the reaction and a chemical "viscosity" is probably admitted to be abortive by all chemists except the De Donder school.

The notation used is consistent, but unattractive. For instance the

symbol μ is used to denote the chemical potential per mole and B is used for the chemical potential per unit mass, for which Gibbs used μ . If a separate symbol were necessary, which is questionable, surely something more appropriate than B might have been used. If this were an isolated instance it would not be worth mentioning, but it is only one of many. When twenty or thirty symbols have to be memorised it is important that they be chosen in such a manner as not to make the memorisation unnecessarily difficult.

Part 2. Les extremes de tension superficielle et l'indifférence des systèmes capillaires.

This monograph contains an exhaustive discussion of the number of degrees of freedom of systems in equilibrium containing curved surfaces. In the special case that all the surfaces are plane this number is given by the familiar "phase rule." The conditions for the surface tension to have a stationary value for constant temperature or for constant pressure or for both constant are derived in detail. It is emphasised that there is no correlation between the composition at which the surface tension is stationary and that at which the total vapour pressure is stationary. Another subject treated exhaustively is the possibility of variations of the amounts of bulk phases and surfaces without any variation of their nature. In fact the exhaustiveness seems rather exaggerated when a mathematical proof is produced that for a variation of the amounts of bulk phases without any variation of their compositions it is essential that there be more than one phase!

There are about 400 formulæ all seemingly correct and all logically deduced. The monograph provides excellent practice for anyone wishing to master the more intricate application of Gibbs' methods to complicated systems.

In one of the few places where the author discusses experimental data he is less fortunate. Referring to Adam and Jessop's measurements of the surface tension of films of myristic acid on aqueous $N/100$ hydrochloric acid, he suggests that these authors ought to have investigated whether there were not sufficient adsorption (presumably negative) of the hydrochloric acid to modify its bulk concentration. A consideration of the order of magnitude of adsorption tells us that an effect of the type suggested would require the ratio surface/volume to be magnified to the order of magnitude met in colloids or porous materials. It would be entirely negligible in Adam's trough. Furthermore such an effect, if present, would have shown itself in that the values obtained for the surface tension would have depended on the depth of liquid in the trough and the experimental results would have appeared unreproducible. As the discussion of these experiments was included for the express purpose of demonstrating the usefulness of the author's formulæ the choice was particularly unfortunate.

The general arrangement of both monographs gives the impression that the parts taken from the author's various papers have been thrown together without sufficient consideration of what would be their natural order. In view of this it is particularly unfortunate that there is no alphabetical index.

Considering the complicated symbols used there are remarkably few misprints in the text and formulæ, though they are rather numerous in the footnotes. The printing is admirable.

E. A. GUGGENHEIM.

ZERO POINT ENERGY IN THE DETERMINATION OF THE STRUCTURE OF SOLIDS.

BY A. R. UBBELOHDE.

Received 14th November, 1935.

I. Covalent and Ionic Linkages.

Substitution of one isotope for another in a solid chemical compound will lead to differences in the vibrational and rotational frequencies of the molecules, without in general changing the function expressing the potential energy of the solid in terms of its structure. Such substitutions will therefore only influence the structure in so far as this is affected by the vibrational and rotational energies of the molecules. The object of the present communication is to point out that the magnitude of the effects to be expected in certain cases should be sufficient to give valuable information on the structure of the solid.

In practice, appreciable differences in vibrational energy are only to be expected in the case of light isotopes, as in changes from deuterium to hydrogen, since the frequency is a function of the reduced mass μ , where $\frac{1}{\mu} = \frac{1}{m_A} + \frac{1}{m_B}$ or $\frac{1}{m_D}$ and m_A is the mass of the other atom or atoms composing the solid. Rotational frequencies, which depend on the moments of inertia of the molecules, will likewise only show an appreciable difference for hydrogen and deuterium compounds, for which the effects to be expected may be summarised as follows:—

Ionic Linkages.—The only lattices in which hydrogen appears as one of the ions are the hydrides of the alkali metals and alkaline earths. These have high melting points, and on electrolysing the molten salt the hydrogen appears at the anode. Lithium hydride has a rock salt structure, the hydrogen playing the part of the chlorine ion; a comparison of LiH and LiD has shown quite an appreciable difference in the lattice dimensions¹

For LiH $a = 4.080 \pm 0.001$.

For LiD $a = 4.060 \pm 0.001$.

It is important to determine whether this difference can be satisfactorily accounted for on grounds of the difference in thermal and null point energy of the two crystal lattices, or whether other factors have to be included. Neglecting atmospheric pressure, the equation of state of the solid may be written²

$$G(V) = YE,$$

¹ Zintl and Harder, *Z. Physik. Chem.*, 1935, 28B, 478.

² Debye, *Physik. Z.*, 1913, 14, 259.

where E is the energy content,

$$G(V) = V \frac{d}{dV} W(V)$$

V is the volume, $Y = \frac{-d \log \nu_m}{d \log V}$, where $W(V)$ expresses the potential energy of the crystal in terms of the volume.

For LiH, ν_m can be calculated from the results of Günther.³ Assuming the validity of Debye's expression for the specific heat,

$$\Theta_{\text{LiH}} = \frac{h\nu_m}{k} = 815^\circ \text{K.}$$

For LiD, where the forces between the atoms are so far as is known identical with those for LiH, but the masses of the vibrating particles differ,

$$\frac{\nu_{\text{mLiH}}}{\nu_{\text{mLiD}}} = \sqrt{\frac{\mu_{\text{LiD}}}{\mu_{\text{LiH}}}} = \sqrt{\frac{16}{9}}$$

and

$$\Theta_{\text{LiD}} = 611^\circ \text{K.}$$

From these two characteristic temperatures the energy content at 293°K. is ⁴

$$\text{For LiH} \quad E - E_0 = 544 \text{ cal./mole.}$$

$$\text{For LiD} \quad E - E_0 = 745 \text{ cal./mole.}$$

The values of E_0 may be calculated assuming a continuous distribution of frequencies of the lattice, ending at ν_m , with $3N$ frequencies in all, as in Debye's theory, *i.e.*—

Number of vibrations between ν and $\nu + d\nu$ is

$$4\pi V \left[\frac{1}{c_1^3} + \frac{2}{c_t^3} \right] \nu^2 d\nu$$

Also

$$3N = 4\pi V \left[\frac{1}{c_1^3} + \frac{2}{c_t^3} \right] \frac{\nu_m^3}{3}$$

Thus, the number of vibrations between ν and $\nu + d\nu$ is $\frac{9N}{\nu_m^3} \nu^2 d\nu$, and the total zero point energy

$$\begin{aligned} E_0 &= \frac{9N}{\nu_m^3} \int_0^{\nu_m} \frac{h\nu}{2} \nu^2 d\nu \\ &= \frac{3}{8} N h \nu_m = \frac{3}{8} R \Theta \end{aligned}$$

$$\text{For LiH at } 293^\circ \text{K.} \quad E = E_0 + 544 = 1820 + 544 = 2364 \text{ cal./mole.}$$

$$\text{For LiD} \quad E = E_0 + 745 = 1368 + 745 = 2113 \text{ cal./mole.}$$

It is clear that the fairly large difference of 452 cal in the zero point energy is already partly compensated at 293°K. by the difference of 201 cal in thermal energy; for crystals with lower Θ than lithium hydride this compensation is still more complete, and masks the effect of changing isotopes, except at lower temperatures.

Without knowing the values of Y and $G(V)$, it is still possible to obtain an estimate of whether this difference of 251 cal between LiH and LiD at 293°K. can account for a difference of 0.020 Å in the lattice dimensions,

³ *Ann. Physik.*, 1920, **63**, 476.

⁴ *Cf. Landolt Bornstein*, Tab. 5th Ed. I., 705.

i.e., an expansion of $0.02/4 = 5 \times 10^{-3}$ per unit length. The thermal expansion of the crystal is due to an increase in E with rise in temperature, and for a specific heat of about 8 cal/mole a difference of 250 cal corresponds approximately with 30° rise in temperature. If the coefficient of expansion of the crystal at room temperature were of the order $5 \times 10^{-3}/30 = 1.7 \times 10^{-4}$, the results would be consistent with the view that the only differences in the lattices arise from differences in vibrational energy content. There seems to be no direct measurement of the coefficient of expansion on record, but even potassium with a much lower melting-point has a coefficient of only 0.8×10^{-4} , so that the value calculated above is rather large. The Debye theory may only be a first order approximation for lithium hydride, however,² and a bigger actual difference of E would require a smaller coefficient of expansion to give the observed change of lattice dimensions on changing the isotopes.

Organic Solids.—Many organic solids are made up of complex molecules whose internal vibrations are almost completely independent of the vibrations of the molecules in the lattice; for such solids the Raman spectrum is practically the same as for the gas, and the heat of vaporisation is small compared with the bonding energies of the individual atoms in each molecule.

Unless the percentage of hydrogen is high, a change to deuterium will not make much difference to the mass of the whole molecule, and will hardly affect the lattice vibrations. Furthermore, the characteristic temperatures will be low, so that any difference in null point energy is practically compensated for by differences in thermal energy at ordinary temperatures. Unless the coefficient of expansion of the solid is abnormally high, the expansion of the lattice on change of isotopes due to the change in lattice vibrations will be small or negligible.

A much more important effect arises from the change in the distance of minimum approach of the molecules (van der Waals, b). So long as the vibrations are simple harmonic, the mean positions in space of the atoms in each molecule remain unchanged, since the function expressing potential energy against separation is generally the same for two isotopes. Owing to the difference in mass the frequency of vibration will, however, differ, and so will the amplitude of oscillation, which corresponds with the difference in zero point energy and thermal energy of the bonds. If there is practically no interaction between the lattice vibrations and the internal vibrations of the molecules, it must be assumed that the minimum distance of approach is conditioned by the amplitude of these internal vibrations.

The magnitude of the change in b on changing from A—H to A—D at a single linkage may be estimated in the case of simple harmonic vibrations. Among the valency bonds, the frequencies AH/AD will be in the ratio $\sqrt{\frac{\mu_{AD}}{\mu_{AH}}}$. The energies for the linkages with H(₁) and D(₂) will be

$$E_1 = \frac{h\nu_1}{2} = 2\pi^2\mu_1a_1^2\nu_1^2$$

$$E_2 = \frac{h\nu_2}{2} = 2\pi^2\mu_2a_2^2\nu_2^2$$

$$\frac{a_1^2}{a_2^2} = \frac{\mu_2\nu_2}{\mu_1\nu_1}$$

² Cf. Blackman, *Proc. Roy. Soc.*, 1934, 148A, 305.

or, since

$$\nu \propto \frac{1}{\sqrt{\mu}}, \quad \frac{a_1}{a_2} = \left(\frac{\mu_2}{\mu_1}\right)^{\frac{1}{2}}$$

For valency vibrations of the C—H bonds

$$\frac{1}{\mu_1} = \frac{1}{12} + \frac{1}{1} = \frac{13}{12}, \quad \frac{1}{\mu_2} = \frac{7}{12}$$

$$\frac{\mu_2}{\mu_1} = \frac{13}{7}$$

and

$$a_1 = 1.168 a_2 \quad a_1 - a_2 = 0.14 a_1$$

also

$$a_1 = \frac{1}{2\pi} \sqrt{\frac{h}{\mu\nu}} \approx \frac{10^{-8}}{\sqrt{\nu}} \text{ cms.}$$

Similar calculations apply to the O—H and N—H bonds, the frequency of the valency vibrations being in each case of the order 3000 cm.^{-1} and the difference in amplitude, or in distance of minimum approach, will be $1.5 \times 10^{-10} \text{ cms.}$, which should in some cases be detectable.

The characteristic temperature of these valency oscillations is about 4000° K. , so that at ordinary temperatures only the zero point oscillation is of significance. For smaller frequencies the difference in amplitude is bigger. This applies particularly to deformation oscillations. Nevertheless, this difference will, in general, have much less influence on the structure of the solid, since a small change in the uncertainty of the valency angle is not of great influence on the neighbouring molecules. Similarly, rotational frequencies, which differ on account of differences in moment of inertia, will only lead to differences of structure in the neighbourhood of transition points, due to molecules such as NH_4^+ or ND_4^+ rotating freely in the crystal.

If the C—H bond is fixed in the crystal, however, the change in distance of minimum approach due to valency vibrations takes place along the valency bond, so that the expansion on changing isotopes should affect the different lattice parameters unequally. In certain cases this may lead to the location of the C—H bond in space. If the benzene molecule is flat, for example, the expansion on changing from C_6D_6 to C_6H_6 due to the above effect should be restricted to the planes in which the molecules are lying in the solid. In the liquid, the effect is averaged over all orientations of the molecules, but the ratio of densities $\text{C}_6\text{D}_6/\text{C}_6\text{H}_6$ should still be somewhat greater than $84/78 = 1.077$, owing to the change in b . The only available data ⁶ for the liquid give a ratio at 17.2° of 1.085, which is in the expected direction, but owing to difficulties of purification this numerical value may have to be altered. (The C_6D_6 was made by polymerisation of C_3D_2).

A much larger difference has been observed between the molecular volumes of liquid hydrogen and deuterium. Using a thermodynamic calculation Clusius and Bartolome ⁷ find for the molecular volumes:—

$$\text{D}_2 (\text{M.P. } 18.66^\circ \text{ K}). \quad \text{H}_2 (\text{M.P. } 13.95^\circ \text{ K}).$$

Solid 20.4_8 c.c.	23.25 c.c.	difference 13.7 percent.
Liquid 23.1_8 c.c.	26.15 c.c.	„ 13.0 „

⁶ Clemo & McQuillen, *J.C.S.*, 1935, 1220.

⁷ *Z. Electrochem.*, 1935, 41, 487.

As would be expected from the fact that H_2 and D_2 rotate freely in the solid near the melting-point, there is no appreciable difference in the per cent. change on melting. The authors ascribe the whole of the difference between D_2 and H_2 to a change of internal pressure resulting from the change in zero point energy, but since their value for the change in internal pressure is 17.3 kg./cm.^2 , this would require for the compressibility of hydrogen the very high value $8000 \cdot 10^{-6}$ per bar. The only experimental value⁸ of 2000×10^{-6} per bar suggests that for liquid hydrogen and deuterium at least part of the volume change is due to a change in b , and the rest to internal pressure changes.

A difference in the minimum distance of approach of H_2O and D_2O has also been suggested as one explanation of the difference in association of the two liquids in dioxan.⁹

Organic Solids Involving Hydrogen and Hydroxyl Bonds, etc.

When some of the linkages between the molecules in the lattice have a binding energy bigger than is due to van der Waals' forces, but smaller than covalent or ionic binding energies, it is no longer adequate to treat the vibrations of the lattice as independent of the internal vibrations of the bonds. At hydrogen or hydroxyl bonds¹⁰ when the H atom is bound with approximately equal energy to two other atoms the change on substituting D requires more complicated analysis, but will in general be smaller than in either ionic lattices, or the organic solids discussed above. The only type studied so far is H_2O and D_2O ,¹¹ where the difference in lattice parameters does not exceed 0.1 per cent. at 0°C . Since the OH groups are certainly not end to end, however, a change in minimum distance of approach even if there were no hydroxyl bond would not be readily detectable.

Summary.

The effect of change of isotopes on the structure of solids is discussed for ionic solids in conjunction with the equation of state of the solid, and for organic solids involving only covalent links in conjunction with the change in minimum distance of approach of the molecules. In some cases the effects should be quite large enough to give definite information on the structure. For ionic solids, the results can be correlated with the distribution of lattice vibrations. For organic solids, the change may lead to the location of C — H bonds in space in some cases.

*The Davy Faraday Laboratory,
The Royal Institution.*

⁸ Eucken, *Verh. Deutsch. Physik. Ges.*, 1916, 11.

⁹ Bell and Wolfenden, *J.C.S.*, 1935, 823.

¹⁰ Cf. Bernal & Megaw, *Proc. Roy. Soc.*, 1935, 151A, 385.

¹¹ Megaw, *Nature*, 1934, 134, 900.

THE VISCOSITIES OF LIQUID MIXTURES.

By K. E. SPELLS, PH.D.

Received 26th November, 1935.

The measurements described here were undertaken with the object of attempting to correlate viscosity with other physical properties. As a subject for such an attempt, any liquid or solution with marked anomalies from the point of view of one property is particularly desirable. In this connection, solutions of isoamyl alcohol in benzene suggest themselves, for the dielectric constant of such solutions presents peculiar features, whose origin is unknown. If the molecular polarisation is plotted against the percentage of alcohol in a solution of isoamyl alcohol in the non-polar solvent benzene, then, according to Lange,^{1, 2} a curve is obtained showing two maxima.

It seemed possible that the graph of viscosity against concentration for the same solution would exhibit corresponding anomalies. All the curves obtained, however, both for isoamyl alcohol and for the solutions of other alcohols in benzene, were quite regular, so that at first the relationship sought did not appear to exist. Nevertheless, before arriving at any definite conclusion, several questions, which will be indicated later, and which will probably form the subject of a later paper, have still to be investigated.

The present paper deals chiefly with an attempt to obtain by a physical argument a mathematical expression to represent the variation of the viscosity of binary liquid mixtures with concentration, the mixtures discussed being not only those on which the measurements described here have been made, but those whose viscosities have been measured by other experimenters.

Measurements.

It was desired in this series of experiments to detect small changes in viscosity with a high degree of accuracy. Special precautions, therefore, had to be taken to preserve the liquid in the viscometer from contamination, and to prevent errors due to evaporation. For these reasons, a viscometer with special features was constructed which allowed a reproducibility in the time of transpiration to within one part in 5000 for the dilute solutions in benzene of the various alcohols investigated, while the accuracy in the cases of more concentrated solutions (of higher viscosity) was only slightly inferior. The time of transpiration in the whole series of experiments varied from 250 secs. to 2000 secs. approximately. An account of this viscometer has been published already,³ so the experimental work may be dealt with very briefly.

The thermostat used was of the usual electric relay type, and it was found to keep the temperature of the apparatus constant to within $\pm 0.1^\circ$ C. Errors due to change of viscosity with temperature were then beyond the limits of detection.

The use of an Ostwald type viscometer necessitates measurements of the time of transpiration and density of both the liquid under consideration and of a standard liquid, benzene in the present case, of which, for purposes of calibration, the viscosity must be known. The values for benzene were

¹ L. Lange, *Z. Physik*, 1925, **33**, 169.

² I. Estermann, *Ergab. exakt. Naturwiss.*, 1929, **8**, 267.

³ E. N. da C. Andrade and K. E. Spells, *J. Sci. Instr.*, 1932, **9**, 316.

taken from the International Critical Tables. The Hagenbach-Couette kinetic energy correction never exceeded 1 part in 450 in these experiments, and was taken into account where necessary. The density measurements were made at the same temperature as the viscosity measurements and, for medium and high concentrations, with the actual solutions. For low concentrations, the densities were measured at concentration intervals of 3 per cent. and the required values obtained by interpolation. The percentage accuracy was greater than that attainable for the transpiration time.

Purity of Materials.

Kahlbaum's "Cryst. Thiophene Free" benzene was used. In the first few experiments, the benzene was specially dried with sodium wire, but as the viscosity was found to be unaffected by this treatment it was discontinued. The *n*-propyl and tertiary butyl alcohols were both treated by refluxing over suitable drying agents and then fractionating. The refractive indices for the H_{α} line of the hydrogen spectrum were used as a criterion of purity in all three cases. The two isoamyl alcohols, α -ethyl propyl alcohol and γ -methyl *n*-butyl alcohol, were used without any further purification, since little appears to be known of their physical properties.

Results of Measurements.

Measurements of the viscosities of solutions of *n*-propyl alcohol in benzene have been made already by Dunstan,⁴ who found a minimum in the viscosity-concentration curve at about 5 per cent. Dunstan, however, did not obtain many points at low concentrations of alcohol in benzene, so experiments were made, taking a larger number of observations, to give a better idea of the form of the curve in the region of the minimum.

The results obtained with solutions in benzene of *n*-propyl alcohol at low concentrations have been published already in graphical form,⁵ but the curve is reproduced here for convenience in Fig. 1.

This curve, together with those given for dilute solutions in benzene of the other alcohols investigated, gives an idea of the accuracy attainable with the form of viscometer used. At the temperature (22° C.) at which the measurements were made, the minimum viscosity is seen to occur at a concentration of 3.1 per cent. of *n*-propyl alcohol in benzene.

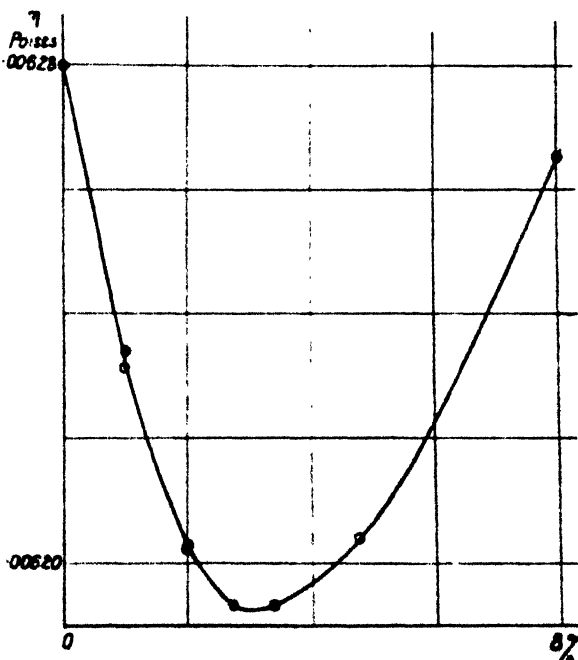


FIG. 1.—*N*-propyl alcohol in benzene—low concentrations.

⁴ A. E. Dunstan, *J. Chem. Soc.*, 1905, 87, 11.

A few readings were taken at the higher concentrations, and the resultant curve over the whole range of concentration (see Fig. 2 (i)), is similar to that obtained by Dunstan.

TABLE I. (FIGS. 1 AND 2 (i)).—VISCOSITIES OF SOLUTIONS OF *n*-PROPYL ALCOHOL IN BENZENE AT 22° C. MAXIMUM DEPARTURE FROM LINEARITY = - 26 PER CENT. AT 50 PER CENT. CONCEN.

Percentage by Wt. of Alcohol.	Density (gms./c.c.).	Viscosity. Poise $\times 10^{-4}$.
0	0.87661	6.28
1.001	0.87565	6.2340
0.997	0.87565	6.2313
1.990	0.87460	6.2025
1.997	0.87460	6.2027
2.003	0.87460	6.2025
2.710	0.87390	6.1934
3.387	0.87325	6.1932
4.762	0.87204	6.2040
8.007	0.86920	6.2653
20.05	0.85933	6.7581
50.12	0.83706	9.7783
89.90	0.80947	18.076
100	0.80247	21.198

The curves obtained for solutions of tertiary butyl alcohol in benzene are shown in Figs. 2 (ii) and 3, while the curves for solutions of the two isoamyl alcohols used, in the same solvent, are given in Figs. 4 and 5.

It will be observed that the curves for all the four different alcohols investigated are very similar in form. In each case there is a minimum value of viscosity, less than that of either component, occurring at a low concentration of alcohol in benzene, while each curve is sagged.

Examination of the curves for the isoamyl alcohols reveals no essential difference of behaviour from that observed in the cases of the *n*-propyl and tertiary butyl alcohols. On this evidence, therefore, there does not seem to be any simple connection between the molecular polarisation and the viscosity coefficient. Before reaching any final conclusion, however, one or two other possibilities have first to be investigated.

Lange, in her paper, is of the opinion that the two maxima she obtained in the graph of molecular polarisation-concentration of isoamyl alcohol in benzene were due to the presence of at least two isomers, the resultant

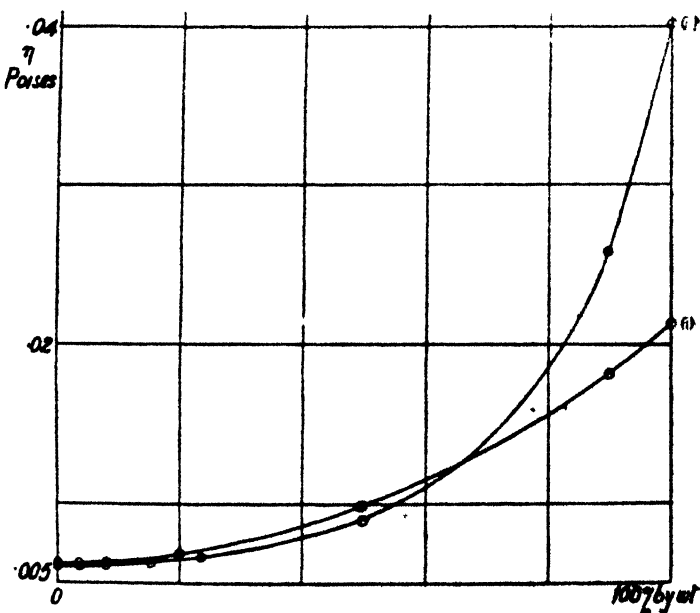


FIG. 2.

- (1) *N*-propyl alcohol in benzene—all concentrations.
- (2) Tertiary butyl alcohol in benzene—all concentrations.

curve being a superposition of two curves, each normal, with their maxima in different positions. Therefore there may still be a relation between molecular polarisation and viscosity, which is not disclosed because the

substances used in the present experiments were possibly much purer, and did not contain more than a trace of any other isomer.

There is, however, another method for the investigation of this question. Recent theoretical work by Andrade⁵ on the subject of liquid viscosity has indicated that investigation of the rate of change of the viscosities of liquids with temperature may prove to be more fruitful in providing knowledge of a fundamental character than the method of comparing the viscosities of different liquids at any arbitrarily chosen temperature. The equation given by Andrade for the variation of the viscosity of a liquid with temperature is

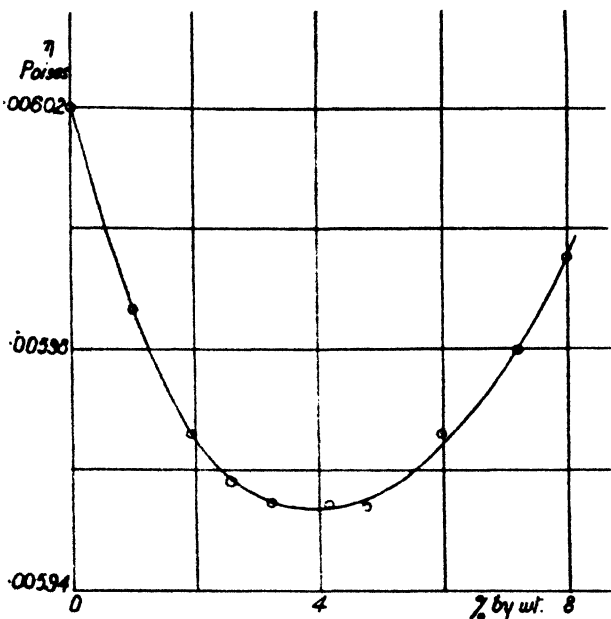


FIG. 3.—Tertiary butyl alcohol in benzene—low concentrations.

$$\eta v^{1/3} = A e^{c/T} \quad (1)$$

where v is the specific volume, η the viscosity at temperature T absolute, and A and c constants to be chosen for a particular liquid. The constant c depends on that part of the potential energy of a molecule involved in the variation of the viscosity of a liquid with temperature (see original paper).⁶

TABLE II.—RANGE = 7.04. MAXIMUM DEPARTURE FROM LINEARITY = - 70 PER CENT. AT 65 PER CENT. CONCEN.

Percentage by Wt. of Alcohol.	Density (gm./c.c.).	ΔM .	$\eta_{calc.}$ ($\Delta M = 75$). Poise $\times 10^{-3}$.	$\eta_{obs.}$ Poise $\times 10^{-3}$.	Percentage Error.
Tertiary Butyl Alcohol in Benzene (25° C.). (Figs. 2 (ii) and 3.)					
0	0.87341	—	6.02	6.02	0
0.998	.87200	—	—	5.9865	—
1.930	.87060	61.5	5.80	5.9658	- 2.78
2.570	.86978	—	—	5.9580	—
3.225	.86885	—	—	5.9545	—
4.162	.86761	64.6	5.717	5.9540	- 3.98
4.759	.86683	—	—	5.9539	—
5.979	.86530	66.0	5.697	5.9660	- 4.51
7.210	.86370	—	—	5.9800	—
8.000	.86270	64.4	5.590	5.9953	- 6.75
15.28	.85465	72.9	6.086	6.2008	- 1.85
23.76	.84600	80.2	6.943	6.5770	+ 5.55
50.08	.82095	79.2	9.363	8.8603	+ 5.68
80.80	.79125	100.6	28.990	25.789	+ 12.4
100	.78462	—	41.905	41.905	0

⁵ E. N. da C. Andrade, *Phil. Mag.* 1934, (7), 17, 497, Supp. and 698.

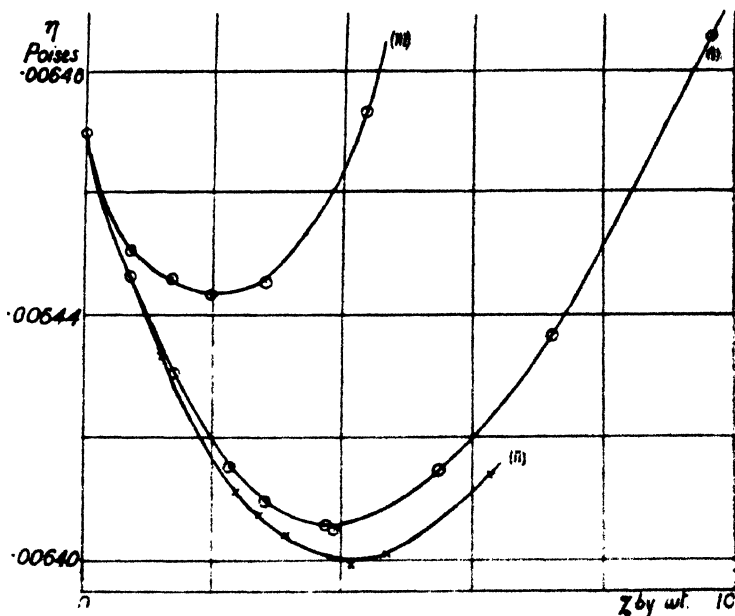


FIG. 4.

- (1) α -Ethyl propyl alcohol in benzene—low concentrations.
- (2) α -Ethyl propyl alcohol (2nd specimen) in benzene—low concentrations.
- (3) γ -Methyl n -butyl alcohol in benzene—low concentrations.

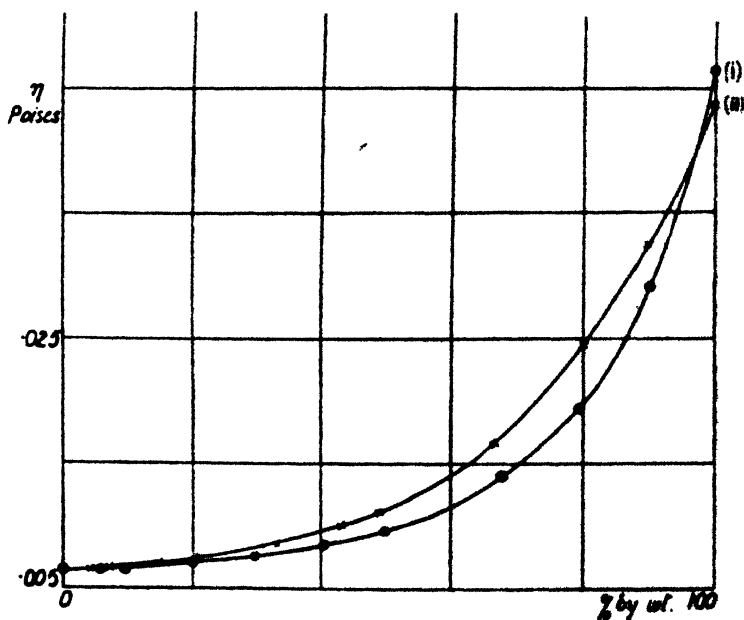


FIG. 5.

- (1) α -Ethyl propyl alcohol in benzene—all concentrations.
- (2) γ -Methyl n -butyl alcohol in benzene—all concentrations.

TABLE III.—RANGE = 7.25. MAXIMUM DEPARTURE FROM LINEARITY = - 57 PER CENT. AT 70 PER CENT. CONC.N.

Percentage by Wt. of Alcohol.	Density (gms./c.c.).	ΔM .	$\eta_{calc.}$ ($\Delta M = 92$). Poise $\times 10^{-2}$.	$\eta_{obs.}$ Poise $\times 10^{-2}$.	Percentage Error.
α-Ethyl Propyl Alcohol in Benzene (20° C.). (Fig. 4 (I) and Fig. 5 (I).)					
0	0.87875	—	0.47	0.47	0
0.716	.87801	86.4	0.4255	0.4463	- 0.32
1.412	.87730	85.3	0.3864	0.4305	- 0.73
2.246	.87648	86.5	0.3539	0.4151	- 0.96
2.813	.87593	86.5	0.3368	0.4096	- 1.13
3.757	.87508	90.5	0.3781	0.4057	- 0.43
3.872	.87500	92.7	0.4169	0.4048	+ 0.19
5.490	.87340	85.3	0.2558	0.4146	- 2.47
7.220	.87194	87.9	0.3184	0.4365	- 1.83
9.640	.86985	89.6	0.4020	0.4855	- 1.28
19.94	.86170	92.2	0.8702	0.8563	+ 0.20
29.71	.85444	90.2	7.2955	7.4293	- 1.80
40.43	.84698	88.5	8.0210	8.3498	- 3.94
49.82	.84094	88.5	9.1981	9.5780	- 3.95
67.90	.83047	90.0	13.750	14.021	- 1.93
79.60	.82456	98.3	20.312	19.431	+ 4.53
90.12	.81969	103.0	30.417	29.204	+ 4.15
100	.81546	—	46.458	46.458	0

Second Specimen (Fig. 4 (II)).

0	.87875		0.47
1.241	.87750		0.4333
2.370	.87638		0.4110
2.741	.87600		0.4410
3.155	.87500		0.4072
4.162	.87470		0.3991
4.690	.87415		0.4010
6.200	.87271		0.4137

TABLE IV — RANGE = 6.75. MAXIMUM DEPARTURE FROM LINEARITY = - 54 PER CENT. AT 55 PER CENT. CONC.N.

Percentage by Wt. of Alcohol.	Density (gms./c.c.).	ΔM .	$\eta_{calc.}$ ($\Delta M = 127$). Poise $\times 10^{-2}$.	$\eta_{obs.}$ Poise $\times 10^{-2}$.	Percentage Error.
γ-Methyl n-Butyl Alcohol in Benzene (20° C.). (Fig. 4 (III) and Fig. 5 (II).)					
0	0.87875	—	0.47	0.47	0
0.700	.87805	92.8	0.3431	0.4503	- 1.66
1.349	.87750	117.8	0.4038	0.4460	- .65
1.950	.87695	115.8	0.3707	0.4433	- 1.12
2.794	.87620	116.5	0.3514	0.4452	- 1.45
4.345	.87490	124.0	0.4356	0.4732	- .58
5.562	.87390	127.5	0.5132	0.5054	+ .12
6.322	.87323	122.9	0.4641	0.5334	- 1.06
6.940	.87275	125.6	0.5246	0.5501	- .39
9.870	.87040	126.4	0.6613	0.6730	- .17
14.64	.86670	127.3	0.9469	0.9346	+ .18
20.44	.86242	130.2	7.4508	7.3213	+ 1.77
23.51	.86015	129.9	7.6963	7.5723	+ 1.64
26.47	.85807	128.5	7.9084	7.8334	+ .96
32.93	.85353	126.1	8.5026	8.5504	- .56
43.05	.84681	124.8	9.9018	10.055	- 1.52
49.00	.84299	125.3	11.021	11.147	- 1.13
66.55	.83247	129.6	16.837	16.614	+ 1.34
80.20	.82481	133.2	24.849	24.378	+ 1.93
90.10	.81947	147.0	33.420	32.448	+ 2.99
100	.81411	—	43.757	43.757	0

It seemed possible, therefore, that the variation of c with the concentration of isoamyl alcohol in benzene might show the anomalies sought.

Measurements of the dielectric constants of solutions of alcohols in benzene are now being carried out in the Physics Department of University College by Mr. Hari Ram Sarna, with the object of comparing values of these constants and of the viscosities obtained with solutions made up from the same specimens. The effect of traces of moisture on the dielectric constants has been found by him to be very marked, and may have vitiated previous results.

An Equation to Represent the Viscosity Variation of a Binary Liquid Mixture with the Concentration of the Components.

A number of empirical formulæ have been proposed by different workers to represent the variation of viscosity with concentration, but only a few of these make any claim to generality, while none, so far as is known to the writer, will fit curves of the type obtained with the solutions of the alcohols investigated here.

It was observed while the measurements given here were being made that the curves, both of viscosity and density, plotted against concentration are sagged; i.e., the viscosity and density at any given concentration are both less than the values which would be given by a linear law. In the case of the density this means that there must be an expansion on mixing the two components of the solution together. Now it is well known that when a liquid undergoes an expansion due to the release of a compression acting on it, this expansion is accompanied by a decrease in its viscosity. It seemed, therefore, of interest to investigate the possibility of there being any connection between the corresponding variations of density and viscosity of a given liquid mixture.

Several investigators have observed the converse phenomenon, that mixtures which exhibit a viscosity maximum also show a definite contraction. McLeod,⁶ however, appears to be the only one to work out a mathematical formula based on this observation. Assuming that a linear law holds for mixtures of components which mix without volume change, and basing his arguments upon considerations of free space, he obtained the following formula, which he found satisfactory for certain mixtures:—

$$\eta = (\eta_1 v_1 + \eta_2 v_2)(0.100/0.100 - C)^{A_1 v_1 + A_2 v_2}$$

where η_1 and η_2 are the viscosities of two liquids present as volume fractions v_1 and v_2 in the mixture, 0.100 is an arbitrary average value chosen in the case of all substances for the free space of both components, and C is the contraction per unit volume deduced from the density of the mixture, while A_1 and A_2 are the arbitrary constants calculated from two sets of data for the mixture.

We now propose to deduce an expression for the viscosity of a mixture, not in terms of free space, but, by using an equation giving viscosity as a function of specific volume, directly in terms of its density. The same initial assumption is made here as in McLeod's attempt, i.e., that a perfect mixture undergoing no volume change on mixing would give a linear law for viscosity-concentration (the relation between the density and concentration, expressed as volume of solute per unit volume of mixture, being, of course, a straight line). There is no real theoretical

⁶ D. B. McLeod, *Trans. Faraday Soc.*, 1923, 19, 17.

justification for this assumption, since the viscosity-concentration curve for an ideal mixture is not known, but it can be defended on general grounds.

To express the viscosity of a liquid as a function of its specific volume at constant temperature, Andrade's viscosity-temperature equation (1) is adapted. If the temperature T be constant, we may write:—

$$\eta = A(I/v)^{1/2} e^{\beta/v}$$

replacing c/T by the constant β .

Suppose, now, that η and ρ be the viscosity and density of a mixture of a given concentration; then, with suitable values of the constants, we have:—

$$\eta = A\rho^{1/2}e^{2\pi} \quad (2)$$

Now if ρ could be altered to the value it would have had, if there had been no alteration of volume on mixing the components together, then, according to the above assumption, η should change to the value calculated from the linear law of viscosity-concentration.

Therefore, if η changes to η_1 when ρ changes to ρ_1 ,

where

$$\rho_1 = \rho_1 + r(\rho_2 - \rho_1),$$

and

$$\eta_k = \eta_1 + r(\eta_3 - \eta_1),$$

r being the concentration by volume of the liquid 2 in the mixture of component liquids 1 and 2, and the suffixes 1 and 2 referring to the appropriate components, then we should have also:—

$$\eta_1 = \frac{\text{surface area}}{\text{volume}} = \frac{4}{3} \rho_1^{\frac{1}{3}} c^{\frac{2}{3}} \rho_1 \quad (3)$$

Dividing (2) by (3), we have : —

$$\eta = \eta_1(\rho/\rho_1)^{1/2} e^{B(\rho-\rho_1)} \quad (4)$$

giving the viscosity of the mixture in terms of its density ρ , the concentration r , and the viscosities and densities of the components 1 and 2, after choosing a suitable value for β . β , from its origin, should depend upon the composition of the liquid in question, whether a mixture or not; and since the composition varies, in the case of a mixture, with the relative proportions of the components present, β should be a function of the concentration. Since, however, there is no way of predicting the variation of β with concentration, we have to make the further simplifying assumption that β is a constant for any particular mixture under investigation. At first sight β might appear calculable from viscosity temperature variation data at different concentrations, but actually this is not possible, since it is doubtful, owing to the somewhat artificial assumptions made in deducing (4), whether there is any simple relationship between β and c .

In order to find the values of β appropriate to any given mixture, values of β are first of all calculated at different concentrations by taking logs of both sides of (4), giving :—

$$\beta.M = \frac{\log_{10} \eta - \log_{10} \eta_1 + \frac{1}{2} (\log_{10} \rho_1 - \log_{10} \rho)}{\rho - \rho_1}$$

M being the modulus of common logs.

A single value of β is then chosen to give the best agreement with observation over the whole range of concentration, bearing in mind that

a difference between the value chosen for β and the actual value calculated will have least effect where the deviation of the density-concentration curve from the linear is smallest.

In the following tables, which are self explanatory, the formula is shown tested first of all against the results obtained by the writer with the solutions in benzene of the particular alcohols investigated here. The formula was not used to fit the results obtained for *n*-propyl alcohol in benzene, since the differences between ρ and ρ_1 were too small at most of the concentrations for the calculations to be made with any degree of certainty (*i.e.*, the graph of ρ against concentration was nearly linear). This seems to indicate that the relation between viscosity and concentration for a binary mixture is not necessarily linear when there is no change of volume on mixing the components, or, at least, that absence of change of volume on mixing is not the only criterion for a perfect mixture. It is interesting to observe, however, that, in the case of *n*-propyl alcohol in benzene, the maximum departure from linearity was much smaller (being only 26 per cent.) than in the cases of the other three alcohols.

TABLE V.—RANGE = 1.37. MAXIMUM DEPARTURE FROM LINEARITY = + 16 PER CENT. AT 40 PER CENT. CONCN.

Percentage by Wt. of Lutidine.	Density.	βM .	$\eta_{calc.}$ ($\beta M = 5$).	$\eta_{calc.}$ Using McLeod's Formula.	$\eta_{obs.}$	Per- centage Error.	Percentage Error Using McLeod's Equation.
Lutidine and Ethyl Alcohol (25° C.).							
0	0.79043	—	0.011536	0.011536	0.011536	0	0
9.97	.80382	7.90	.01141	.01146	.011499	— 0.77	— 0.34
19.88	.81972	5.17	.01162	.01164	.011643	— 0.20	0
39.77	.85142	5.90	.01178	.01188	.012023	— 2.02	— 1.19
59.70	.88029	5.23	.01126	.01133	.011328	— 0.60	0
79.43	.90743	4.38	.01033	.01041	.010204	+ 1.23	+ 2.06
90.55	.92101	6.77	.009516	.00950	.009686	— 1.75	— 1.92
100	.93218	—	.0087766	.0087766	.0087766	0	0

In view of the fact that the formula deduced has but one constant, as against the two arbitrary constants of McLeod, the agreement between calculated and observed results for the alcohol-benzene mixtures, on which the measurements described here were made, seemed sufficiently good to justify the trial of (4) against results obtained by other observers.

It was decided therefore to make tests on some of the mixtures against which McLeod tried his two constant formulæ; these being particularly suitable for the purpose since they give results as different as possible from those obtained here, showing maxima instead of minima in the viscosity-concentration curve. Also, McLeod's equation appears to be the only one having any extensive application to mixtures.

Several of the mixtures studied by McLeod have been selected at random, and equation (4) has been fitted to their viscosity-concentration curves. As may be seen from the tables, the single-constant expression deduced here is reasonably successful when considered in the light of what has been accomplished so far in this direction. In general it may be claimed that it fits the facts nearly as well as the two-constant expression of McLeod.

In one case, the fit has been improved by assuming that β varies linearly with concentration r * according to the relation

$$\beta = \beta_1 r + \beta_2 (1 - r),$$

equation (4) then becoming an equation with two arbitrary constants:—

$$\eta = \eta_1 \left(\frac{\rho}{\rho_1} \right)^{\frac{1}{2}} e^{\{\beta_1 r + \beta_2 (1-r)\}(\rho - \rho_1)} \quad . \quad . \quad . \quad (4')$$

TABLE VI.—RANGE = 3.38. MAXIMUM DEPARTURE FROM LINEARITY = + 220 PER CENT. AT 40 PER CENT. CONCEN.

Percentage by Wt. of Alcohol.	Density.	βM .	$\eta_{calc.}$ ($\beta M = 14.5$).	$\eta_{calc.}$ Using McLeod's Formula.	$\eta_{obs.}$	Per- centage Error.	Percentage Error Using McLeod's Equation.
0	0.99973	—	0.01308	0.01308	0.01308	0	0
10	.98393	24.25	.01785	.01770	.02179	- 18.1	- 18.8
20	.97252	17.20	.02715	.02600	.03165	- 14.2	- 17.8
30	.95977	15.40	.03802	.03720	.04050	- 6.12	- 8.15
40	.94238	14.46	.04398	.04390	.04390	- 0.18	0
50	.92162	13.86	.04398	.04320	.04180	+ 5.22	+ 3.35
60	.89927	13.55	.04037	.03870	.03770	+ 7.08	+ 2.65
70	.87602	13.39	.03499	.03268	.03268	+ 7.07	0
80	.85197	14.54	.02705	.02620	.02710	- 0.18	- 3.32
90	.82654	12.96	.02194	.02040	.02101	+ 4.42	- 2.91
100	.79784	—	.01466	.01466	.01466	0	0

Ethyl Alcohol and Water (10° C.).

TABLE VII.—RANGE = 2.70. MAXIMUM DEPARTURE FROM LINEARITY = + 127 PER CENT. AT 80 PER CENT. CONCEN.

Percentage by Wt. of Acid.	Density.	βM .	$\eta_{calc.}$ ($\beta M = 8.5$).	$\eta_{calc.}$ ($\beta M = 13.17$ + 4.1(1-r)).	$\eta_{calc.}$ Using McLeod's Equation.	$\eta_{obs.}$	Percentage Error Using $\beta M = 8.5$.	Percentage Error Using $\beta M = 13.17$ + 4.1(1-r).	Percentage Error Using McLeod's Equation.
0	.9992	—	0.01134	0.01134	0.01134	0.01134	0	0	0
10	1.0142	8.05	.01380	.01287	.01285	.01368	+ 0.88	- 5.92	- 6.07
20	1.0284	7.43	.01699	.01526	.01520	.01626	+ 4.49	- 0.15	- 6.52
30	1.0412	7.45	.02017	.01833	.01860	.01897	+ 6.32	- 3.37	- 1.95
40	1.0523	7.46	.02308	.02179	.02143	.02143	+ 7.70	+ 1.68	0
50	1.0615	7.88	.02538	.02560	.02490	.02416	+ 5.05	+ 5.90	+ 3.06
60	1.0685	8.52	.02670	.02901	.02784	.02682	- 0.45	+ 8.15	+ 3.81
70	1.0733	9.60	.02681	.03130	.02935	.02935	- 8.67	+ 6.65	0
80	1.0748	11.23	.02520	.03068	.02813	.03068	- 17.8	0	- 8.31
90	1.0713	13.72	.02138	.02579	.02340	.02786	- 23.2	- 7.43	- 16.0
100	1.0553	—	.01410	.01410	.01410	.01410	0	0	0

Acetic Acid and Water (15° C.).

* To conform with McLeod's work, the calculations have been performed with r expressed as concentration by weight in Tables V., VI., and VII.

A better fit could certainly be obtained in the cases of most of the mixtures investigated by the introduction of a second arbitrary constant in this manner. This is to be expected, since, as has been mentioned, β should vary with concentration, but the assumption of a linear variation has no theoretical support. In fact, in the only cases where $(\rho - \rho_1)$ is determined with sufficient accuracy for smooth curves of β -concentration to be obtained, these curves show a distinct minimum. This suggests that β might be replaced more profitably by non-linear functions. It seems probable, then, that the nature of the variation of β with concentration for a particular mixture will depend upon certain properties of the components; but until it is known what these properties are, no useful purpose will be served by introducing additional complications in equation (4).

I should like to take this opportunity to express my thanks to Professor E. N. da C. Andrade for suggesting the original problem and for his continued interest and help throughout the course of this work. My thanks are also due to the Department of Scientific and Industrial Research for a grant extending over part of the time during which the work described here was being done.

Summary.

Accurate measurements of the viscosities of solutions of four alcohols in benzene have been made.

In an attempt to correlate viscosity with the dielectric constant, the results obtained for the viscosities of the solutions of two isoamyl alcohols in benzene have been examined for anomalies corresponding to those obtained in the case of the dielectric constants. The curves of viscosity plotted against concentration do not exhibit any peculiarities, but, before reaching a conclusion, a new method, suggested here, of investigating the problem must be tried.

An equation with one arbitrary constant has been deduced to give the viscosity of a binary liquid mixture in terms of its density. This equation has been tested against the measurements given here, and also against results obtained by other workers.

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THE EXTINCTION COEFFICIENTS OF IODINE AND OTHER HALOGENS.

BY E. RABINOWITCH AND W. C. WOOD.

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In order to extend the experiments on the photochemical equilibrium in halogens¹ to iodine, we required the knowledge of the extinction curve of iodine vapour. Despite the great number of investigations dealing with the spectrum and photochemical properties of gaseous iodine, its extinction was measured only once, by Vogt and Koenigsberger.² They used saturated vapour at 48° C. and 88° C., and over-

¹ E. Rabinowitch, H. L. Lehmann, *Trans. Faraday Soc.*, 1935, **31**, 689.

² K. Vogt, J. Koenigsberger, *Z. Physik*, 1923, **13**, 300.

heated vapour at 400° C. Bonhoeffer and Harteck³ computed the extinction curve of iodine using the values found by Vogt and Koenigsberger at 88° C. Some of our experiments pointed to this curve being incorrect, or, at least, not applicable to iodine vapour at room temperature. The extinction coefficients seemed to be at least twice the values given by the curve. Referring to the original paper, we found that, by using the measurements at 48° C. extinction coefficients 2, 3 or even 6 times greater are obtained. Some of them appeared to us to be rather too high. We considered it therefore advisable to re-measure the whole extinction curve, using iodine vapour at room temperature.

Extinction Curve of Iodine.

The experimental arrangement consisted of a 1000 c.p. pointolite lamp run on a 220 V. battery supply, a lens projecting an image of the incandescent plate into the centre of a quartz absorption cell 12 cm. long, and a second lens forming an image of the plate on the slit of a monochromator.

A Hilger VI spectrograph was used at first, with a selenium iron photocell (Electrocell) connected to a Zernicke galvanometer (Z3, sensitivity, 1.5×10^{-10} amps. per mm.). The photocell, with a slit in front of it, slid along a scale in the focal plane of the spectrograph. A violet filter (Wratten No. 39) was used in front of the slit for measurements below 5000 Å., in order to suppress scattered light.

In later experiments we were able to use a quartz double monochromator (Hilger D 129). The photocell was fixed behind its exit slit. The results obtained with both instruments were in good agreement.

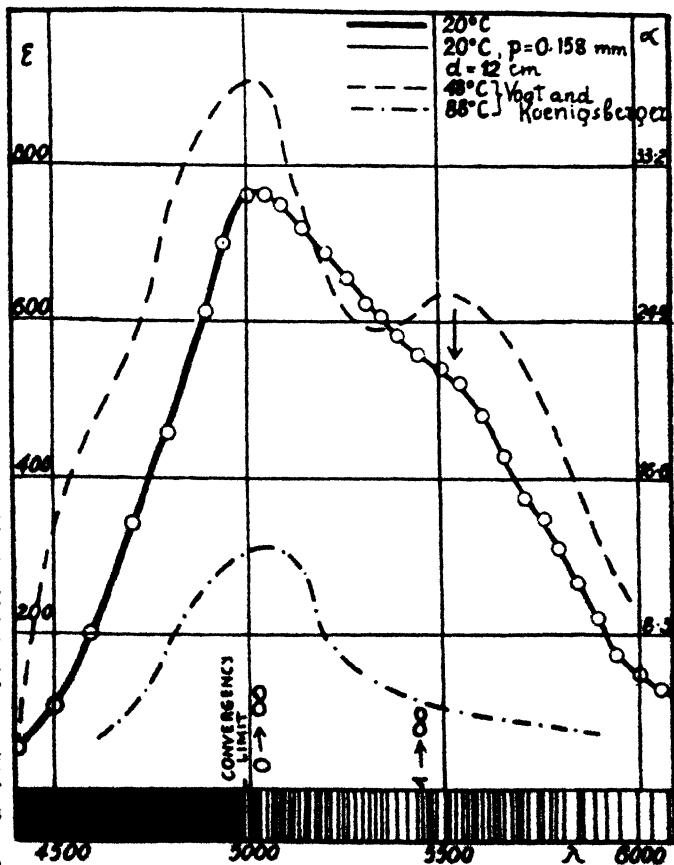


FIG. 1.—Extinction-curves of iodine vapour.

³ K. F. Bonhoeffer, P. Harteck, *Grundlagen der Photochemie*, 1933, p. 89.

Iodine vapour was introduced from a container kept at about 19°C. , into the thoroughly evacuated absorption cell, of which the temperature was about 20°C. , and the cell closed by a stopcock lubricated with phosphoric acid and graphite. The density was taken from the known vapour pressure curve of iodine,⁴ and roughly controlled by means of a manometer filled with sulphuric acid. The intensity of light transmitted through the cell was measured at different wave-lengths, first with iodine vapour in the cell and then with the vapour removed by touching the wall with a piece of cotton wool soaked in liquid air. The operation required less than a minute and the light intensity of the lamp was sufficiently constant to make the results absolutely reproducible. The exactness of the measurements was between 20 per cent. at 4300 \AA (where the absorption was less than 2 per cent.) and 2 per cent. at 5000 \AA (where about 20 per cent. of light was absorbed in the cell). Curve A, Fig. 1, shows the measured values. The left-hand scale of ordinates corresponds to concentration measured in mols. per litre, the right-hand one to pressures in atmospheres at 20°C. Curves B and C in Fig. 1, are derived from the measurements of Vogt and Koenigsberger, the upper at 48°C. , the lower at 88°C. Confirming our expectations, the extinction curve of iodine at room temperature was found to lie between the two curves of Vogt and Koenigsberger, and nearer to the upper one.

Dependence of the Extinction on Temperature.

We made no measurements at higher temperatures, and are therefore unable to say positively that one (or both) of the curves of Vogt and Koenigsberger are incorrect. The change of the extinction coefficient with temperature which is suggested by these curves is, however, a very unusual one; they are supposed to increase by about 30 per cent. between 20°C. and 48°C. , and then to decrease so rapidly that the values at 88°C. become three, or even six, times smaller than those at 48°C.

The dependence of the extinction curve on temperature has been investigated by Gibson and Bayliss⁵ in the case of chlorine. They found a gradual decrease in the height of the maximum (attaining — 30 per cent. at 765°C.) accompanied by an increase in extinction on both sides further away from the maximum. This behaviour was quantitatively explained by Gibson, Rice and Bayliss⁶ as being due to an excitation of the first vibrational level of the Cl_2 molecule.

A similar flattening and broadening of the extinction curve with rising temperature was observed in bromine vapour by Ribaud,⁷ and in iodine solution in hexane by Gr6h and Papp.⁸ Their results must be explained in the same way—by an increase in the number of vibrating molecules of bromine and iodine. By virtue of the Franck-Condon principle, the absorption by the molecules in the first vibrational state produces two absorption maxima, situated on both sides of the main maximum due to the absorption by non-vibrating molecules. The existence of these two "humps" was shown by Gibson, Rice and Bayliss

⁴ The reliability of this curve is very essential for the exactness of the extinction coefficients calculated in this paper. The data of J. P. Baxter, C. H. Hickey, and W. C. Holmes, *Trans. Amer. Chem. Soc.*, 1907, 29, 127, seem to be trustworthy, and agree well with those of F. Haber and F. Kerschbaum, *Z. Elektrochemie*, 1914, 20, 302. Our own measurements, however rough, showed no marked discrepancies with the data of Baxter, Hickey and Holmes.

⁵ G. E. Gibson, N. S. Bayliss, *Physic. Rev.*, 1933, 44, 188.

⁶ G. E. Gibson, O. K. Rice, N. S. Bayliss, *Physic. Rev.*, 1933, 44, 193.

⁷ G. Ribaud, *Annales de physique*, 1919, 9, 11, 178.

⁸ T. Gr6h, St. Papp, *Z. physik. Chem.*, 1930, 149A, 153.

by analysing the empirical extinction curve of chlorine. In the cases of bromine and of iodine, in which the vibrational quanta are smaller and more molecules are excited at room temperature, the humps on the red side of the maximum are easily recognisable on the curves (see the arrows in Figs. 1 and 3). In the case of iodine vapour (Fig. 1), the comparison with the band spectrum shown below, clearly indicates the hump as due to the superposition on the main band series of a second series, coming from the first vibrational state.

It is noteworthy that these humps appear in *solutions* of Br_2 and I_2 as well, showing that the vibrational quanta of these molecules are not strongly affected by dissolution in carbon tetrachloride and similar solvents.

Effects of Concentration and Foreign Gases.

Vogt and Koenigsberger supposed that the differences between the extinction coefficients determined at different temperatures are due to differences in concentration rather than in temperature. One has to distinguish sharply between two regions in the spectrum of iodine. Below 4990 Å., the spectrum is continuous, and no deviations from Beer's law are expected theoretically (this prediction was confirmed, e.g., by measurements with bromine). Above 4990 Å., the spectrum consists of lines (where the true extinction coefficients are very high) and intervals between them, where the extinction drops to zero. The extinction curve which one obtains experimentally in this region actually depends on concentration, thickness of the absorption cell and width of the slit. (With a very narrow slit, a zig-zag line must be obtained instead of a smooth curve.) With rising concentration of iodine, two effects occur simultaneously. *Firstly*, the *lowering* of the mean extinction coefficient with growing absorption, which is always observed when mean extinction coefficients are determined with non-monochromatic light covering a region where the true extinction coefficients are strongly variable. (To observe this, without the second effect, it is best to change the thickness of the absorption cell instead of changing the pressure.) *Secondly*, the *increase* in the mean extinction coefficient due to the broadening of the lines.⁽⁶⁰⁾ (To isolate this effect, it is best to add foreign gas instead of increasing the pressure of iodine itself.) The first effect falsifies the results, making the extinction curve dependent on special conditions of the experiment; the second effect restores the true shape of the extinction curve (at least so long as the influence of the foreign gas is confined to a change in the *shape* of the absorption lines and does not affect the absolute transition probability).

In order to obtain a curve showing correctly the average extinction coefficients in the band region, it is necessary to work with a sufficiently wide slit, covering a range containing several bands, and either use very low iodine pressures (or a correspondingly short light-path) or to add enough of the foreign gas to paralyse the effect of the higher iodine concentration. The correctness of the curve is ensured as soon as the extinctions in the centres of the lines become small enough to be representable by a linear instead of an exponential function.

⁽⁶⁰⁾ This effect was investigated by F. W. Loomis and H. O. Fuller, *Physical Review* [2], 1932, 39, 180, in iodine vapour, and by V. Kondratjew and L. Polak, *Z. Physik*, 1932, 76, 386, in bromine vapour.

In Fig. 1, the *dotted* curve in the region above 5000 Å. is the one we obtained by using a 0.5 mm. slit (covering regions from 50 to 100 Å. wide) with iodine at a pressure $p = 0.157$ mm., and a light path $d = 12$ cm. This is only one of the many curves which may be obtained in this region; even the strange shape of the upper curve in Fig. 1, with its minimum at 5300 Å. may be due to effects of this kind. The differences between this curve, and our curve at $\lambda < 5000$ Å. cannot, however, be explained in this way, and still less can concentration effects account for the smallness of the extinction coefficients found by Vogt and Koenigsberger at 88° C.

Since it is difficult to measure very low absorptions exactly, the

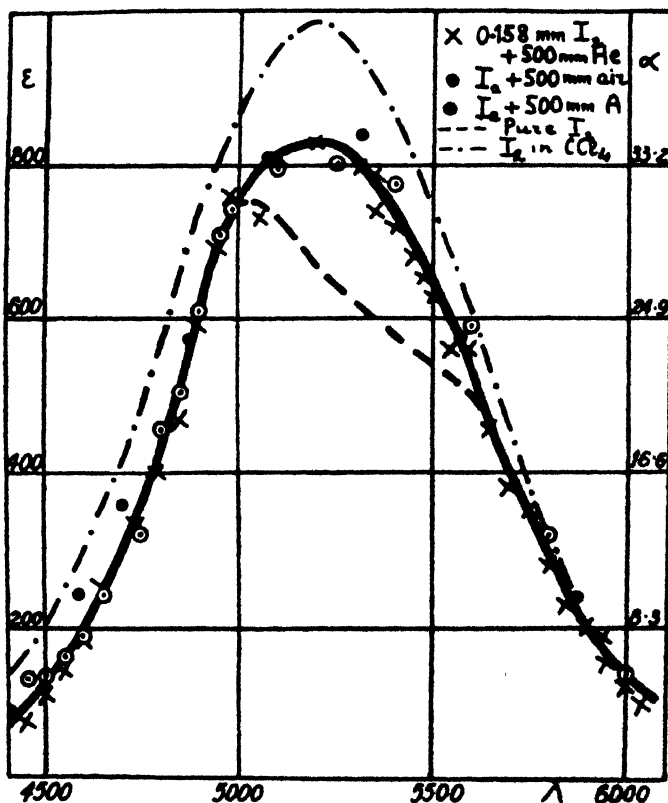


FIG. 2.—The "limiting" extinction-curve of iodine.

between 5000 and 5500 Å., this causing the shifting of the maximum from 5000 to 5200 Å. The decrease in the pressure effect above 5500 Å. indicates that in this region the true extinction coefficients are not very high, even in the centres of the lines, and therefore no sensible increase in absorption is caused by broadening of the lines.

The increased absorption in the region 5000-5700 Å. is the cause of the fact that iodine vapour in an air-filled vessel appears more deeply coloured than vapour of the same pressure in an evacuated container.

It is noteworthy that the influence of the three gases helium, argon and air is the same—at least at the high pressure of 500 mm. used. This, together with the observation that no sensible increase in absorption

the easiest way to obtain the correct mean extinction curve of iodine in the band region is to use iodine vapour with inert foreign gases. Fig. 2 shows the results we obtained by adding 500 mm. of helium, argon or air to 0.157 mm. of iodine. According to expectations, the continuous region remains unaffected, but the mean extinction coefficients in the band region are considerably increased, especially between

can be attained by a further increase in pressure, are indications that the extinction curve obtained in this way does not differ appreciably from the "limiting" curve corresponding to the ideal case of very low iodine pressure or complete line broadening.

The uppermost curve in Fig. 2, shows the extinction coefficients of iodine dissolved in carbon tetrachloride, according to Gillam and Morton.⁹ The shape of the curve and the position of the maximum are the same as in the "limiting" curve for iodine vapour. The slight increase in the absolute values of the extinction coefficients will be discussed in the next section.

Influence of Solvents on the Absorption Spectra of the Three Halogens.

In Fig. 3, the extinction curves of all three halogens in the gaseous state at room temperature¹⁰ are compared with those of their solutions in carbon tetrachloride.¹¹ In the case of bromine, the greatest part of the spectrum (below 5100 Å.) and in the case of chlorine practically the whole of it are regions of continuous absorption. Accordingly, dissolution in a "neutral" solvent does not change the general shape of the

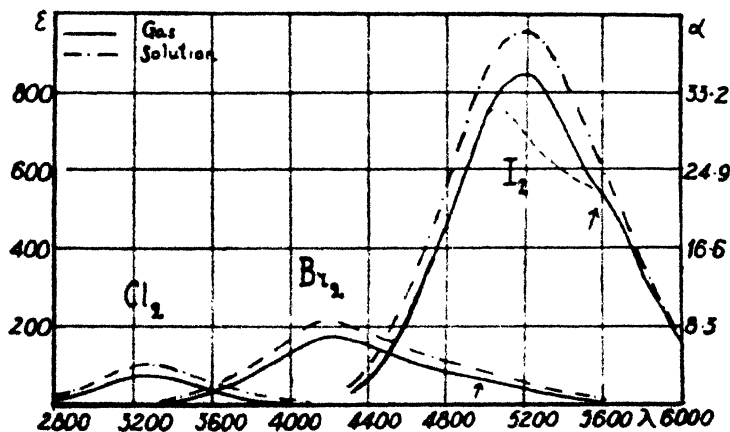


FIG. 3.—The extinction-curves of the three halogens in gas and solution.

extinction curves, nor the position of the maxima. The other effect of the solvent mentioned above is, however, clearly shown by these curves; The *absolute values* of the coefficients (i.e., the corresponding transition probabilities) are increased by about 50 per cent. and more in the case of chlorine and up to 30 per cent. in the case of bromine; the corresponding effect in iodine is of the order of 15-20 per cent.¹¹

⁹ A. E. Gillam, R. A. Morton, *Proc. Roy. Soc.*, 1929, 124, 604.

¹⁰ The data for chlorine gas are by Gibson and Bayliss,⁴ for bromine by Ribaud.⁷ We tested some points of this last curve and found the data of Ribaud confirmed.

¹¹ The curves for the solutions are those given by Gillam and Morton.⁹ We use them because these authors give data for all three halogens. If the curves given by Gróh and Papp,⁸ or O. S. Walker, *Trans. Faraday Soc.*, 1935, 31, 1435, for I_2 in CCl_4 are used instead of the curve by Gillam and Morton, the differences between the gas curve and the solution curve for I_2 become still smaller. It is deplorable that the extinction curves for I_2 solutions given in Landolt Börnstein's *Physikalisch Chemische Tabellen*, 5th edition, Vol. II., p. 894, are in error by a factor 10. Together with the wrong curve for the I_2 vapour they lead us to the belief that the extinction of iodine in solution is 50 times greater than that of iodine vapour whereas in truth they are nearly identical.

The explanation of this effect must be sought in the nature of the electronic transitions involved. They are of the "intercombination" type $^1\Sigma \rightarrow ^3\Pi$. Transitions involving a change of multiplicity are not allowed in very light atoms and molecules and become gradually easier with increasing atomic weight, due to a stronger interaction between spin and orbital momentum (e.g., a complete absence of intercombination lines in the spectrum of helium and the high intensity of the well-known resonance line 2536 Å. of mercury). This rule explains the increase in the absolute intensity of the absorption bands of the halogens in the series Cl_2 , Br_2 , I_2 (the maximum values of ϵ being 90, 160 and 740 respectively). The same cause must be responsible for the action of the solvent on the spectra of these three halogens. The electric fields of the surrounding molecules weaken the selection rules—an influence which is known from the appearance of many "prohibited" lines in the Stark effect of atomic spectra. This influence is strongest with chlorine, and becomes very weak in iodine, where the selection rule is already made ineffective by the interaction of spin and orbital momentum in the molecule itself.

Summary.

(a) The *extinction coefficients of iodine vapour at room temperature* are measured between 4300 and 6200 Å. They are found to be 2 to 6 times greater than the values generally in use.

(b) The *influence of temperature upon the extinction* is discussed. Small humps observed on the extinction curves of bromine and iodine are shown to be due to absorption by vibrating molecules.

(c) The *influence of the density* is discussed. It is shown that the correct mean extinction curve in the band region can be obtained either by using a very low iodine pressure or—more conveniently—by adding an inert gas. Measurements are made with helium, argon and air, at 500 mm. The absorption in the continuous part of the spectrum is found to remain unaffected by the foreign gas, but the mean extinction coefficients in the band regions are considerably increased. The "limiting" extinction curve of iodine vapour obtained in this way has a maximum at 5200 Å., and a shape resembling that of the extinction curve of iodine dissolved in carbon tetrachloride.

(d) The *influence of the solvent upon the extinctions of the three halogens* is compared. The extinction coefficients are appreciably increased by dissolution, especially in the cases of Cl_2 and Br_2 . This is explained as being due to a molecular Stark effect enhancing the probability of the singlet-triplet intercombination, especially in light atoms.

We sincerely thank Professor F. G. Donnan, F.R.S., for his interest in this work, and Dr. O. Walker for valuable discussions.

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PROPERTIES OF ILLUMINATED IODINE SOLUTIONS. I. PHOTOCHEMICAL DISSOCIATION OF IODINE MOLECULES IN SOLUTION.

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In this paper experiments will be described the purpose of which was to obtain direct evidence of the primary photochemical process in solutions of halogens. The experiments consisted in measurements of the change in the concentration of iodine-molecules in strongly illuminated solutions.¹

Experimental.

The arrangement was described in a previous paper,¹ and is shown schematically in Fig. 1. A rectangular glass cell A (20 × 100 mm.), con-

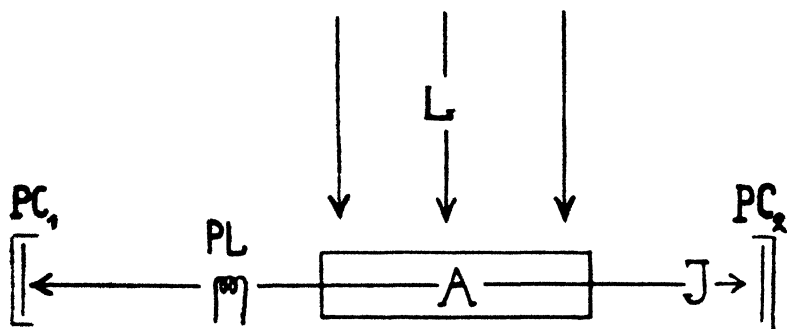


FIG. 1.—Scheme of the apparatus.

taining the iodine-solution, was substituted for the vacuum cell used in the previous work with gases. Automatic carbon arc (25 amps) was used for illumination ("illuminating light," intensity L). In cases where especially high light intensity was wanted, a 120 amps search-light with a 20-inch parabolic mirror was substituted. The change in the extinction-coefficient of the solution caused by illumination was measured by a photoelectric compensation device consisting of a 6V., 24W. lamp PL ("photo-cell light," intensity I), and the two selenium iron photo-cells PC1 and PC2. The details can be found in the above-mentioned paper.

Previously, we used the apparatus with gases. Since in solutions the effect is much smaller, it was necessary to increase further the sensitivity of the method. By improving all conditions relevant to the mechanical and optical stability of the apparatus, and by replacing one of the photo-cells by a new one with higher internal resistance, we were able to measure intensity changes of the order of 2×10^{-4} (0.002 per cent.) instead of 1×10^{-4} attained in our previous work. This accuracy proved to be sufficient for the detection of the dissociation effect in solutions, thanks to favourable conditions: the thermal effects, which were the chief source of trouble in experiments with gases, cause much less trouble in liquids.

¹ The same effect was previously investigated in gaseous bromine, see E. Rabinowitch and H. L. Lehmann, *Trans. Faraday Soc.*, 1935, 31, 689.

Although their theoretical magnitude is not much smaller, the time necessary for the establishment of thermal equilibrium is considerably larger (of the order of 100-1000 secs.) because of the high heat capacity of the liquid. Since the readings are taken a few seconds after the beginning of the illumination, the thermal effects are practically avoided.

On the other hand, we encountered an unexpected difficulty in keeping the intensity of the photo-cell light constant with a liquid in the path of the beam. Besides the quick fluctuations of the photo-current of the order of 0.002 per cent. which are also observed in working with gases, and are probably due to slight variations in the lamp voltage, we observed slower "drifts," often changing the intensity by as much as 0.1 per cent. They are relatively weak with aqueous solutions, but especially strong

with carbon tetrachloride. This indicates that they are due to thermal convection currents in the liquid, the dependence of refractivity on temperature being especially strong in the case of CCl_4 . We were obliged to eliminate them by the method used in the previous work, i.e., taking a great number (usually 60) single readings and averaging them. Fig. 2 shows the results of a typical set of measurements. It represents the successive readings of the galvanometer, taken alternatively with closed and opened shutter between the arc and the absorption cell. The effect for which we were searching is clearly recognizable, although superimposed on

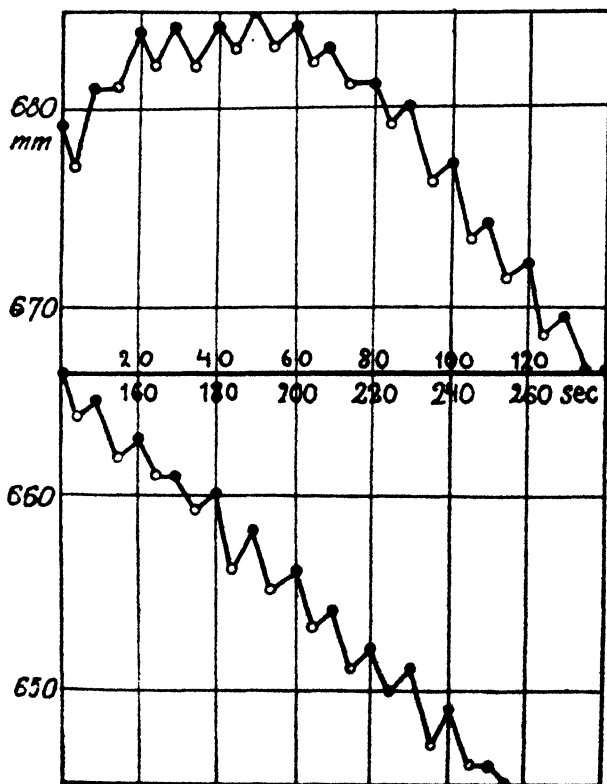


FIG. 2.—The dissociation-effect in iodine solution. Points show the extinction of the solution in the dark, circles that during illumination.

quick fluctuations of the current as well as on a slow drift. The total photo-current in this particular experiment was 2×10^{-4} amps, its variations due to the dissociation effect were about 3×10^{-10} amps (0.015 per cent.) and the drift over 5 mins. about 0.15 per cent.

Results.

Experiments were made with iodine dissolved in CCl_4 , C_6H_{14} , CS_2 , CH_3OH and H_2O , and with bromine in CCl_4 . Only the solutions of iodine in carbon tetrachloride and hexane gave the "positive" effect shown in Fig. 2. In all the other solutions a "negative" effect was observed

instead, *i.e.*, an increase in the extinction-coefficient during illumination. This negative effect will be dealt with in a separate paper. Here we are concerned with the positive effects in CCl_4 and C_6H_{14} only.

The measurements give (a) the total intensity of the light falling upon the photo-cell I , and its change ΔI , due to illumination; and (b) the intensity of the illuminating light L (measured by a thermophile-galvanometer system calibrated with a standard lamp). From the relative change of transmission, $\frac{\Delta I}{I}$, the relative change on the concentration of I_2 -molecules, $\Delta[\text{I}_2]/[\text{I}_2]$, is calculated. Instead of the method described previously,¹ we now used the following relation:—

$$\frac{\Delta I}{I} = \frac{\Delta[\text{I}_2]}{[\text{I}_2]} c_{(\text{I}_2)} \bar{\epsilon}_l d \ln 10 \quad (1)$$

where d is the length of the cell, $\bar{\epsilon}_l$ the mean extinction coefficient of the solution for the photo-cell light, $c_{(\text{I}_2)}$ the concentration of iodine molecules in mols per litre (units used in defining ϵ), and $[\text{I}_2]$, the same in number of molecules per c.c. Relation (1) is exact for monochromatic light only. The photo-cell light was filtered through an infrared absorbing glass, a green filter (Wratten No. 55) and a $\text{Cu}(\text{NO}_3)_2$ solution. The spectral region transmitted was 4900–5200 Å., and the mean extinction coefficient was $\bar{\epsilon} = 736$. (The maximum extinction coefficient of iodine in CCl_4 is 890, at 5180 Å). It remained practically constant for absorptions between 10 per cent. and 85 per cent., thus justifying the use of relation (1).

The same approximation (use of a mean extinction coefficient $\bar{\epsilon}_l$) was used for the calculation of N_{hv} , the number of quanta absorbed per sec. in 1 c.c. of solution. Three sets of filters were used:—

Filters.	Spectral Region Transmitted.	Maximum at	$\bar{\epsilon}_l$ (± 10 per cent.).
1. 1 cm $\text{Cu}(\text{NO}_3)_2$ (25 per cent. sol.) + Wratten No. 32.	4000–5100	4000	325
2. 1 cm. $\text{Cu}(\text{NO}_3)_2$ (25 per cent.)	4000–5300	5000	625
3. Jena glass filter gg11 + 1 cm. $\text{Cu}(\text{NO}_3)_2$ diluted	5000–5800	5400	550

Because of the inconstancy and inhomogeneity of the light from the arc, the values of $\bar{\epsilon}_l$ were determined by using the small lamp FL as light source (disregarding the fact that the intensity of distribution in the light of a glowing filament must be somewhat different from that in the light of a carbon arc, even in the narrow spectral regions concerned). The use of a mean coefficient $\bar{\epsilon}_l$ was admissible, despite the wide range of the true ϵ_l values involved (ranging from 100 at 4400 Å up to 890 at 5180 Å) because of the smallness of the total absorption across the cell (which was usually of the order of 10 per cent.).

The N_{hv} values were calculated by means of the following formula:—

$$N_{hv} = \frac{6.14 \times 10^3 \times 10^{-30}}{19.7 \times 10^{-17}} L \bar{\epsilon}_l C_{(\text{I}_2)} \times 1.13(1 + 2.3 \bar{\epsilon}_l C_{(\text{I}_2)}) \\ = 8.11 \times 10^{10} (1 + 2.3 \bar{\epsilon}_l C_{(\text{I}_2)}) L \bar{\lambda} \quad (2)$$

where 6.14×10^3 is the calibration factor of the thermopile; L the intensity of the illuminating light (deflection of the galvanometer in cm.); $1.13 \times (1 + 2.3 \bar{\epsilon}_l C_{(\text{I}_2)})$ are correction factors accounting for the reflexion losses and for the absorption between the middle and the back wall of the cell. The factor $\bar{\lambda}/19.7 \times 10^{-17}$ ($= \lambda/hc$) expresses the intensity by the number of quanta; the expression

$$6.14 \times 10^3 \times 1.13(1 + 2.3 \bar{\epsilon}_l C_{(\text{I}_2)}) L \bar{\lambda} / 19.7 \times 10^{-17}$$

represents thus the number of quanta passing a sq. cm. in the middle of the cell per second; on multiplying it by

$$\bar{\epsilon}_l C_{(\text{I}_2)} \ln 10 = 2.30 \bar{\epsilon}_l C_{(\text{I}_2)},$$

we obtain the number of quanta absorbed per second in 1 c.c.

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Table I. gives the summary of the results. Column 6 shows the number of quanta absorbed, column 10 the corresponding change in the concentration of iodine molecules.

In order to make clear the meaning of the results, we first consider those obtained by variation of one independent variable only.

TABLE I.

Exp. No.	$c(I_2) \times 10^5$ mols./l.	λ (Å.)	i_L	L (cm.)	$N_{\text{abs}} (\times 10^{14})$	$I \times 10^4$ (ampere).	$\Delta I \times 10^4$ (ampere).	$\Delta I / I$ (per cent.).	$\Delta(I_2) / I_2$ (per cent.).	$[I] \times 10^{-13}$ (molecules per c.c.).	$\epsilon \times 10^4$
A. Iodine in Carbon Tetrachloride.											
101	2.2	4700	325	15.5	4.2	9.4	2.75	0.0029	0.0087	2.3	1.0
101	8.8	4700	325	19.5	15.7	2.9	1.75	0.60	0.45	4.8	1.4
101	11.0	4700	325	12.5	18.1	2.1	1.45	0.60	0.41	5.4	1.25
103	4.4	5000	625	41.7	49	7.5	6.15	0.0082	0.0123	6.5	2.3
104	4.4	5000	625	43	51	7.5	6.65	0.89	1.33	7.05	2.1
104a	4.4	5000	625	43	51	8.8	6.15	0.70	1.05	5.05	3.2
104a	8.8	5000	625	42	104	3.6	5.7	158	118	12.5	1.35
104a	13.2	5000	625	34.5	133	1.7	2.6	154	0.70	11.9	1.9
104b	13.2	5000	625	35	134	1.7	2.25	132	0.66	10.5	2.4
105	4.4	5000	625	42	49	4.3	5.25	122	182	9.6	1.05
105	8.8	5000	625	37	92	2.0	1.75	0.87	0.65	6.85	3.9
105	8.8	5000	625	37.5	92	2.9	2.65	0.42	0.69	7.35	3.4
105	8.8	5500	550	37.5	84	2.9	2.55	0.0088	0.0066	7.0	3.4
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)
B. Iodine in Hexane.											
111	2.6	4700	325	11.5	3.8	9.7	2.6	0.0027	0.0064	2.0	1.0
121	4.0	4700	325	33	17.0	3.3	3.05	111	183	8.8	0.85
121	4.0	4700	325	42.5	21.5	5.7	4.05	0.71	1.17	5.6	1.4
122	5.9	4700	325	29.5	22.5	5.7	2.95	0.52	0.56	3.95	2.85
109	6.4	5000	625	37.5	64	5.0	6.4	0.0128	0.0132	10.2	1.25
109	12.8	5000	625	38.5	142	1.9	2.85	149	0.77	11.8	2.05
111	2.6	5000	625	35	24	9.7	8.05	0.89	225	7.0	1.0
111	2.6	5000	625	15	10	9.7	5.25	0.54	1.37	4.25	1.1
111	4.3	5000	625	42.5	49	8.4	6.8	0.81	1.24	6.4	2.4
111	4.3	5000	625	39.5	46	7.6	6.5	0.86	1.32	6.8	2.0
111	4.3	5000	625	18.5	21	7.6	4.35	0.57	0.87	4.45	2.1
111	9.6	5000	625	39	10.9	3.2	3.6	112	0.76	8.7	2.8
123	5.9	5000	625	143	23	5.0	11.3	226	252	17.5	1.5
123	5.9	5000	625	49	7.9	5.0	4.75	0.95	1.06	7.5	2.8
111	9.6	5500	550	37.5	82	3.2	3.45	0.0108	0.0074	8.5	2.25
121	4.0	5500	550	65	68	5.8	11.7	202	332	15.8	0.55
122	5.9	5500	550	90.5	141	5.7	15.2	266	297	21.0	0.65
122	5.9	5500	550	18.5	29	5.7	4.65	0.82	0.91	6.4	1.4
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)

Dependence of the Effect on Light Intensity.

In Table II. we compare the results obtained by variation of the number of quanta, N_{abs} , the concentration $c(I_2)$, and wave-length λ being kept constant.

TABLE II.—DEPENDENCE OF THE EFFECT ON LIGHT INTENSITY.

$$\frac{\Delta[I_2]}{[I_2]} = \text{const} \times N^x.$$

Exp.	$c(I_2) \times 10^3$ mols./l.	$N_{hv} \times 10^{15}$	$\frac{\Delta[I_2]}{[I_2]} \times 10^4$	x
111 (C_6H_{14})	2.6	2.4	2.25	0.57
		1.0	1.37	
	4.3	4.6	1.32	0.54
		2.1	0.87	
122 (C_6H_{14})	5.9	14.1	2.97	0.75
		2.9	0.91	
123 (C_6H_{14})	5.9	23.0	2.51	0.80
		7.9	1.00	

Table II. shows the law $\frac{\Delta I_2}{I_2} = \text{const} \sqrt{N_{hv}}$ to be the best approximation. Exps. 122 and 123 were made with the 120 amps. search-light, giving a more powerful but much less constant and uniform illumination than the 25 amps. arc. used in exp. 111. The results are therefore less exact than those of exp. 111, which conforms exactly to the square root law.

Dependence of the Effect on Iodine Concentration.

Table III. shows the results obtained by changing the concentration $C(I_2)$, keeping L as constant as possible. The exponents y are in the neighbourhood of -0.5 ; only exp. 111 suggests a proportionality with $1/c(I_2)$ rather than with $1/\sqrt{c(I_2)}$.

TABLE III.—DEPENDENCE OF THE EFFECT ON IODINE CONCENTRATION.

$$\frac{\Delta[I_2]}{[I_2]} = \text{const} \times c(I_2)^y.$$

Exp.	L (cm.).	$[I_2] \times 10^3$ mols. l.	$\Delta[I_2]/[I_2] \times 10^4$.	y .
101 (CCl_4)	14	2.2 8.8 11.0	0.87 0.45 0.41	$\left. \begin{array}{l} -0.5 \\ -0.5 \end{array} \right\}$
103 104 105 (CCl_4)	40	4.4 8.8	$\left. \begin{array}{l} 1.23 \\ 1.33 \\ 1.05 \\ 1.32 \end{array} \right\} \text{mean}$ $\left. \begin{array}{l} 1.36 \\ 0.84 \end{array} \right\}$ $\left. \begin{array}{l} 1.18 \\ 0.65 \\ 0.69 \end{array} \right\} \text{Mean}$	$\left. \begin{array}{l} -0.7 \\ -0.4 \end{array} \right\}$
109 (C_6H_{14})	38	6.4 12.8	1.32 0.77	$\left. \begin{array}{l} -0.8 \end{array} \right\}$
111 (C_6H_{14})	40	2.6 4.3 9.6	2.25 1.32 0.76	$\left. \begin{array}{l} -1.0 \\ -0.7 \end{array} \right\}$

Discussion.

We attribute the illumination effects observed in iodine solutions in carbon tetrachloride and hexane to a dissociation of iodine molecules into atoms. The stationary concentration of atoms must be equal to twice the number of I_2 molecules disappeared :

$$[I] = 2\Delta[I_2]. \quad (3)$$

The values of $[I]$ are calculated in column (11) of Table I. They are of the order of 10^{-11} mols. per c.c. (corresponding to 10^{-10} mols per litre).

The velocity with which the atoms are formed is :—

$$+ \frac{d[I]}{dt} = 2\gamma N_{hv} \quad (4)$$

The velocity of their recombination (assuming the simple mechanism $I + I \rightarrow I_2$) is given by

$$- \frac{d[I]}{dt} = c[I_2], \quad (5)$$

and the stationary state by

$$[I] = \sqrt{\frac{2\gamma N_{hv}}{C}} \quad (6)$$

Formula (6) differs from formula (30) in our previous paper, (i) by the factor γ before N_{hv} , accounting for the possibility of the quantum yield of dissociation being < 1 , due to the "primary recombination" discussed by Franck and Rabinowitch,² and (ii) by the disappearance of the factor $[X]$ (concentration of foreign molecules acting as third bodies) because of the presence of the molecules of the solvent at each double collision between two iodine atoms in solution.

According to (6), the stationary concentration of iodine atoms must be proportional to $\sqrt{N_{hv}}$; and since the absorption is (roughly) proportional to the concentration $[I_2]$, also to $\sqrt{[I_2]}$, the relative effect $\frac{\Delta[I_2]}{[I_2]}$ must therefore be proportional to the square root of the light intensity \sqrt{L} , and to the inverse square root of concentration, $1/\sqrt{[I_2]}$. These predictions are in accordance with the results shown in Tables II. and III.

The velocity constant C cannot be calculated from the experiments, but only the quotient C/γ . The results are given in column (12) of Table I. The constancy of the results is not unsatisfactory, considering the extreme smallness of the effects measured. The mean values of C/γ are given in Table IV. :—

TABLE IV.—VELOCITY CONSTANTS OF THE RECOMBINATION OF I-ATOMS.

Solvent.	C/γ .	C'/γ .	γ_{av} .
C_6H_{14}	1.7×10^{-10}	6.1×10^{21}	2.4×10^{-10}
CCl_4	2.3×10^{-10}	8.2×10^{21}	1.7×10^{-10}

C is the velocity constant for concentrations measured in molecules per c.c., C' the same for concentrations in mols per litre.

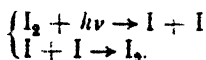
² J. Franck and E. Rabinowitch, *Trans. Faraday Soc.*, 1934, 30, 120.

The constants C/γ can be compared with that obtained previously for the recombination of bromine atoms in helium gas at atmospheric pressure. This was:—

$$C_1 \left(= \frac{C}{[\text{He}]} \right) = 7.5 \times 10^{-23}.$$

For atmospheric pressure, $[\text{He}]$ is 2.7×10^{19} , and C becomes 2×10^{-13} ; whereas the corresponding constant in solution is of the order of 10^{-10} , according to Table IV. (and assuming that γ is, if not equal to 1, at least of the order of 0.1 to 1). *The velocity of recombination of atoms in solution is thus about 500 times greater than in a gas at atmospheric pressure.* This result is in accordance with the assumption that triple collisions are necessary for the recombination in gas, and that practically each collision is a recombining one in solution.

The dependence of the effect on light intensity, its dependence on iodine concentration and its absolute order of magnitude are thus all three in agreement with theory and support the explanation of the effect as being due to the simple mechanism.



Something remains to be said about the coefficient γ . The simplest possible assumption is $\gamma = 1$. (This assumption cannot be *exactly* correct, because of the occurrence of the "primary recombination." The extent of this latter effect is however not yet known.) No clear trend of γ is revealed by comparing the effects observed in different spectral regions:—

$\bar{\lambda}$:	4700	5000	5400 Å
$\overline{C/\gamma}$ in C_6H_{14}	1.75	1.9	1.2
$\overline{C/\gamma}$ in CCl_4	1.4	2.4	

In the second column about one-half, and in the third nearly the whole, of the absorbed quanta belong to the spectral region which is discontinuous in iodine vapour. We must thus assume, that in solution the quantum yield of dissociation in this region is the same as below 5000 Å, whereas in a sufficiently diluted gas this yield is $\gamma = 1$ below and $\gamma = 0$ above this limit. These results indicate, that dissociation of excited I_2 molecules (and *not* dissipation of the excitation energy by collisions of the second kind) is the chief cause of the disappearance of the iodine fluorescence in solutions. The mechanism of dissociation must be the one discussed theoretically by Van Vleck³ and illustrated by Fig. 3. The excited molecules in the state $^3\Pi_{0+}$ usually return by fluorescence into the ground state $^1\Sigma$. In the inhomogeneous electric field of the surrounding molecules, a transition from the state $^3\Pi_{0+}$ into the state $^3\Pi_{0-}$, which is a "prohibited" one in the case of isolated molecules, becomes possible. Once in the state $^3\Pi_{0-}$, the molecule becomes unstable and dissociates.

If the quantum yield γ is supposed to be $= 1$ in solution throughout the absorption spectrum, then the values of C/γ in Table I. represent the actual velocity constants C of the recombination reaction, and we may use them for calculating the mean lifetime of the free atoms τ (or their collision numbers $s = 1/\tau$, although this quantity has not much meaning for atoms which are supposed to recombine at their very first collision).

³ J. H. van Vleck, *Physic. Rev.*, 1932, 40, 544.

In the last column of Table IV., the life periods τ_0 are calculated for $t = 0^\circ \text{C.}$, and a concentration corresponding to the pressure $p = 1 \text{ atm.}$ in a gas. They are of the order of $2 \times 10^{-10} \text{ sec.}$

With the aid of the usual kinetic formula for the calculation of the collision-number in gases, the mean time-interval between two collisions in a gas with a collision diameter $\sigma = 5 \times 10^{-8} \text{ cm.}$ (a plausible value for the beginning of the interaction between two iodine atoms according to Fig. 3), is found to be :—

$$\tau_{0(\text{gas})} = 1.5 \times 10^{-10} \text{ secs.}$$

The practical identity between this value of $\tau_{0(\text{gas})}$ and the values of $\tau_{0(\text{solution})}$ calculated above suggests the following simple assumptions concerning the mechanism of the process under discussion :—

(1) *The quantum yield of dissociation of I_2 molecules in solutions is in fact practically equal to unity throughout the absorption spectrum.*

(2) *The collision intervals of iodine atoms in solution are the same as calculated for iodine atoms in gas according to the kinetic theory. Each collision is a "recombining" one.*

This explanation would mean that "primary recombination," i.e., recombination of the atom-pair produced by absorption before its actual separation by diffusion—does not play an important rôle—at least in the case of I_2 -solutions. The only important influence of the solvent upon the

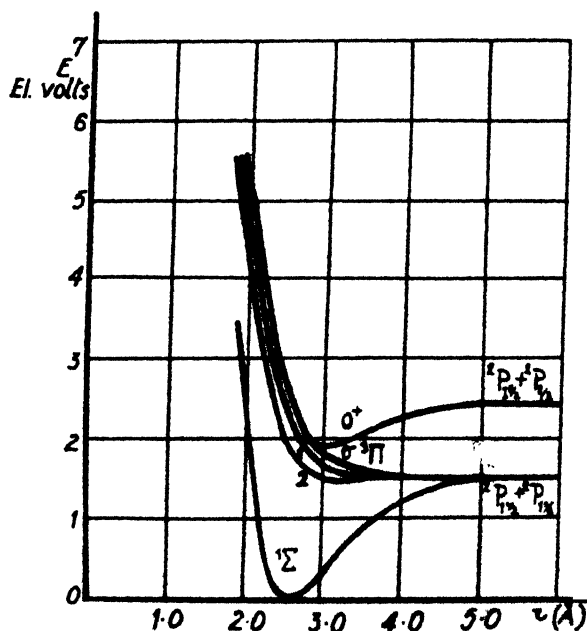


FIG. 3.—Potential curves of the I_2 -molecule according to van Vleck.

primary photo-chemical process consists in enabling a dissociation to occur in the spectral region where fluorescence is the only effect in sufficiently diluted gases.

This conclusion is, however, not at all a necessary one. An alternative explanation is made possible by a general assumption which will be discussed more fully elsewhere, and which postulates that: if, for two particles just in contact with each other in solution, the chance to separate without another collision is equal to $1/n$, then the average time-interval between separation and subsequent collision with another dissolved particle, is n times greater than the corresponding collision interval in a gas.

For the case in question, this assumption leads to the possibility of the following explanation :—

(I.a) *The quantum yield of the dissociation of I_2 -molecules is $\gamma = \frac{1}{n} < 1$.*

(II.a) *The mean life time of the free atoms $\tau_{0(\text{solution})}$ is n times greater than the collision interval $\tau_{0(\text{gas})}$ in a mono-atomic iodine gas.*

The product $\gamma\tau_{0(\text{solution})}$ remains in this way equal to $\tau_{0(\text{gas})}$.

The assumptions (I.a) and (II.a) would be improbable, if γ and τ_0 were two independent quantities. But, according to the above-mentioned general proposition, the same cause which decreases γ (by "primary recombination") increases the mean lifetime τ_0 in the same proportion. Further experiments are therefore necessary to ascertain the actual part played by the primary recombination in the photochemistry of iodine solutions.⁴

In the above-mentioned paper,² the dissipation of energy by collisions of the second kind with the solvent ($I_2^* + CCl_4 \rightarrow I_2 + CCl_4$) was mentioned as a second possibility which may decrease the quantum yield of dissociation in solutions. For this loss of light-energy, however, no natural compensation by a prolonged life of free atoms can be expected. We may thus conclude, that the experimental results obtained with iodine in carbon tetrachloride and hexane, leaving open a possibility of energy-losses by primary recombination, show definitely the absence of important losses by energy-dissipation through second-kind collisions during the activated state of the I_2 -molecule.

Summary.

(a) By improving a photochemical compensation apparatus described previously, it was possible to measure extinction changes of the order of 0.002 per cent.

(b) By means of this apparatus, the reversible change of the extinction-coefficient of iodine-solutions under the influence of strong illumination was detected and measured.

(c) In the case of iodine solutions in carbon tetrachloride and hexane the effect consists in a decrease in the extinction coefficient, and is due to a dissociation of I_2 molecules into atoms. Its dependence on light intensity and on I_2 -concentration are in accordance with this explanation.

(d) The recombination velocity of iodine atoms in solution is about 1000 times greater than that of bromine atoms in helium at atmospheric pressure, in accordance with the assumption that triple collisions are necessary for recombination in gas, and that each collision is a recombining one in solution.

(e) The quantum yield of dissociation of I_2 -molecules in solution is the same in the spectral region below 5000 Å, which is continuous, and above 5000 Å, which is a band region in I_2 gas.

(f) The results can be explained in two ways:—

Either by the assumption that the quantum yield of I_2 dissociation in solution is equal to 1, and the average lifetime of free atoms equal to the average collision interval in a monoatomic iodine-gas; or by the assumption that the quantum yield is $1/n < 1$ (due to so-called "primary recombination") and the free lifetime of the atoms n times longer than the collision interval in the gas.

(g) Losses of energy by dissipation through collisions of the second kind between activated I_2 molecules and molecules of the solvent do not occur to an appreciable extent.

⁴ Any argument against primary recombination which is based on an estimation of the stationary concentration of free atoms in illuminated solutions is, according to this reasoning, fallacious. This applies, for instance, to the remarks made by Ogg on the occasion of the Symposium of Photochemistry held in San Francisco, 1935 (*Chemical Reviews*, 1935, 17, 423).

(h) In a number of solutions of I_2 and Br_2 , the extinction coefficients were found to increase reversibly during illumination. This "negative" effect will be dealt with separately.

Our sincere thanks are due to Professor F. G. Donnan, F.R.S., for his encouraging interest in this work and the hospitality he has generously shown us in the Sir William Ramsay Laboratories.

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QUANTITATIVE EXPERIMENTS ON EMULSIFICATION BY ULTRASONIC WAVES.

BY C. BONDY AND K. SÖLLNER.

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Two previous papers ¹ dealt with the mechanism of emulsification by ultrasonics in the systems: organic liquids in water and *vice versa*, and mercury in water and organic liquids. It appeared that the behaviour of organic liquids ("oils") had to be distinguished from that of mercury. In the case of oils emulsification was due to the collapse of cavitations produced by the ultrasonics at the interface of the two liquids. In that of mercury, drops of the other liquid driven into the mercury cause thin metal films to burst, thus forming small drops owing to the high interfacial tension.

In this paper some quantitative results are discussed concerning the nature of those emulsions, produced under different conditions.² Two points are of special interest: the amount dispersed under different conditions and the degree of dispersion.

A standard method of emulsifying is obvious in order to obtain reproducible and comparable results. Such a method is not easily realised; even when allowing for only a small degree of accuracy. The main difficulty is that the degree of emulsification depends on the mechanical vibration-energy, and the latter depends on several factors which are hard to control: a small difference in the thickness of the walls of the vessel used,³ the relative positions of the vessel and the vibrating quartz

¹ C. Bondy and K. Söllner, *Trans. Farad. Soc.*, 1935, 31, 835, 843.

² Conf. preferably W. T. Richards, *J. Am. Chem. Soc.*, 1929, 51, 1724; H. B. Bull and K. Söllner, *Koll. Z.*, 1932, 60, 263; M. Reggiani, *C.R.*, 1933, 200, 123.

³ The sound energy transmitted through a solid wall depends upon the thickness of the latter; cf. e.g., Lord Rayleigh, *Theory of Sound* (1896), Vol. II., p. 86; R. W. Boyle and G. B. Taylor, *Physic. Rev.*, 1926, 27, 518; R. W. Boyle, *Science Progress*, 1928, 75; E. Hiedemann and H. R. Asbach, *Physik. Z.*, 1933, 34, 734. But, as with test tubes the main part of the energy is transmitted by transverse vibrations of the glass walls and not by longitudinal waves in the latter. (Cf. also S. J. Sokoloff, *Elektr. Nachr.-Techn.*, 1929, 6, 454, and N. N. Malov and S. N. Rechevkin: *Hochfrequenztechn. u. Elektroak.*, 1932, 40, 134. The thickness of the glass is not so critical as might otherwise be expected. As thick walled tubes have a much smaller tendency than thinner walled ones to vibrate transversely, it is advisable to choose tubes of a moderate wall thickness, made from a high quality glass and well annealed, otherwise they are liable to break and thus to spoil the oilbath.

plate,⁴ the position of this plate between the electrodes, etc., may cause marked differences. Further, it is impossible to perform the experiments under isothermal conditions; the temperature of the liquids rises more rapidly with increasing degree of dispersion, because heat is evolved, especially at interfaces.⁵ This heat effect cannot be counterbalanced, even if the oilbath is cooled with streaming water. Yet, the formation and the properties of an emulsion depend upon temperature. Again, there is no satisfactory method available for direct measurement of the energy of high frequency sound waves. The only known factor is the amount of energy, characterised by the electric current, which enters the vibrating circuit.⁶ Finally, the mechanical output may vary to a certain extent whilst the energy remains constant.

We do not claim that the experiments hereafter recorded have been carried out under, in any way, optimum conditions, but the conditions were those which in laboratory use proved to be good and convenient. The result—the first quantitative data to be published on emulsions prepared by ultrasonic waves—may nevertheless be of some interest, and they give suitable information on the general efficiency of this method.

Experiments have shown that the concentration of an emulsion produced, when maintaining the external conditions of the vibrating system as nearly the same as possible, did not vary⁷ more than 20 per cent. This indicates how far the external conditions may be reproduced; yet this is only true, if the experiments are performed by the same experimenter who always dips the tubes in the same way into the oil fountain.

The experiments were carried out with 3 c.c. water, plus 3 c.c. of oil and 5 c.c. of liquid and 0.5 c.c. of Hg respectively, in test tubes of about 15 mm. internal diameter.

1. Water-Oil Systems.

(a) Some Semi-Quantitative Data on Water-Oil and Oil-Water Emulsions.

As the main interest of this communication is not so much concerned with the nature of a great variety of emulsions, but mainly with the manner in which emulsions change with the conditions mentioned above, only semi-quantitative experiments with different substances were carried out; 3 c.c. of 1N. KCl solution (to exclude as far as possible differences due to a different charge of the different substances used in this series), and 3 c.c. of oil were irradiated in "thick-walled" test tubes of Monax glass, having an internal diameter of about 15 mm. The energy was only indicated by the strength of the current entering the secondary circuit (110 millamps. in this series). (Some further details relating to the energy question may be found in an earlier paper.⁸) The concentration of the emulsions was estimated from their opacity, a method which was proved to be satisfactory. The results are found in Table I.

The stability of the emulsions is moderate. The concentration is distinctly smaller after several hours. The droplets in both emulsions cream up or settle down respectively and unite with the coherent phases. The

⁴ W. T. Richards and A. L. Loomis, *J. Am. Chem. Soc.*, 1927, 49, 3086.

⁵ R. W. Wood and A. L. Loomis, *Phil. Mag.* (VII.), 1927, 4, 417.

⁶ H. Freundlich, F. Rogowski and K. Söllner, *Kolloidchem. Beihfte*, 1933, 27.

223.

⁷ W. T. Richards, *loc. cit.*, also assumes the maximum error to be 20 per cent. With stabilised Hg emulsions our values were even less reproducible.

water phase is usually quite clear after standing over night, the oil phase in most cases, the viscosity playing an important rôle. With suitable stabilisers very concentrated and stable emulsions may be obtained.

Similarly, many organic liquids, or more correctly their saturated solutions, may be emulsified in each other.

(b) Quantitative Measurements on Emulsions of Toluene in Water.

As a standard example for more thorough investigation, toluene-in-water emulsions was chosen, and the results obtained here may fairly accurately also hold for a great many other similar substances.

TABLE I—CONCENTRATION OF OIL—WATER AND WATER—OIL—EMULSIONS. ENERGY 110 MILLIAMPS. TIME OF IRRADIATION 1 MINUTE

Substances.	Degree of Opacity of Water Phase	Degree of Opacity of "Oil" Phase
H ₂ O—Benzene	+	+
H ₂ O—Toluene	++	+
H ₂ O—Xylene	++	+
H ₂ O—Cyclohexane	++	+
H ₂ O—Tetrahydronaphthalene (Tetralin) (techn.)	+++	++
H ₂ O—Dekahydronaphthalene (Dekalin) (techn.)	+++	++
H ₂ O—Petroleum ether	Very poor	Very poor
H ₂ O—Paraffin oil	++	+
H ₂ O—Carbontetrachloride	++	+
H ₂ O—Chloroform	+	++
H ₂ O—Tetrachlorethane	++	++
H ₂ O—Tetra-chloro-ethylene	++	++
H ₂ O—Bromoform	+++	+
H ₂ O—Bromonaphthalene	+++	+
H ₂ O—Nitrobenzene	+++	+
H ₂ O—Aniline	+++	+
H ₂ O—o-Toluidine	+++	+
H ₂ O—Amyl alcohol	++	Poor
H ₂ O—Cyclohexanol	++	Very poor
H ₂ O—m-Cresol	++	+
H ₂ O—Ethyl acetate	+	Very poor
H ₂ O—Ethyl-acetoacetate	++	+
H ₂ O—Ether	Nil	Nil
H ₂ O—Oleic acid	+++	+

In Table II. (a) the concentrations of the toluene-water emulsions obtained with varying time and energy of irradiation are recorded.

3 c.c. of toluene (pure, sulphur-free) and 3 c.c. of normal distilled water were irradiated in thick-walled (about 1 mm.) test tubes of Monax glass, having an internal diameter of about 15 mm. The concentration of the emulsion was calculated from its density, the latter being determined by means of a pycnometer. A fresh tube was used in every experiment. Hence, one may conclude from Table II. (a), to a certain extent, how far the results are reproducible; for instance, whether experiments performed with a constant energy show a regular trend. The energy was, as usual, only indicated by the strength of the current (in milliamps) entering the secondary circuit.

In pure emulsions (not containing emulsifiers) it was to be expected that the concentration would rapidly reach a limiting value: the rate of emulsification becoming equal to the rate of coagulation, i.e., the rate with

which the droplets unite to larger ones and coalesce with the bulk of the oil. This limiting value is 4.2-4.5 per cent. (per volume), when using high energies; with 80 milliamps it is reached in 3 minutes, with 115 milliamps in 30 seconds. Obviously, the rate of formation increases strongly with increasing energy; hence, it is surprising that the limiting value for 115 milliamps is not higher than that for 80 milliamps. We must conclude, from this fact, that the rate of coagulation also increases with rising energy. Below 50 milliamps the energy is not sufficient to cause emulsification. At 50 milliamps the limiting value is low.

With high energies (115 milliamps) the concentration decreases, when irradiating for a longer period. This is probably due to an effect caused by an increase of temperature, perhaps also to the degassing of the liquid. High temperature is disadvantageous for emulsifying, by ultrasonics (the collapse of the cavities being less pronounced), and moreover favours coagulation.

These "oils," e.g., toluene are mostly distinctly hydrophobic, and the emulsions which they form with water on shaking, without addition of

TABLE II - CONCENTRATIONS

Energy in Milliamps.	Disperse Phase in Vol. Per Cent.								
	Time of Irradiation in Minutes								
	½	1	2	3	5	10	15	30	
(a) Toluene - Water - Emulsions.									
50	-	0.0	-	-	0.5	—	1.8	1.8	
80	1.1	2.3	3.1	4.1	3.9	—	4.2	—	
115	3.5	4.5	3.9	—	3.1	2.8	2.7	—	
(b) Toluene/Sodium Oleate—Solution.									
50	-	1.4	2.4	—	—	11	—	23	32
80	—	2.0	4.5	12	18	—	39	45	—
115	—	Entire amount emulsified up to concentration of 75 per cent							

emulsifiers, so far as they are stable at all,* are very dilute. Emulsions produced by ultrasonic waves are much more concentrated; evidently the factors causing dispersion are more powerful than in the case of shaking and stirring.

The degree of dispersion was determined in the following manner: a small amount of the emulsion was diluted with 5 to 10 times its volume of a 2 per cent gelatin solution. A drop of this stabilised emulsion was brought on to an object slide (having a cavity) and held for 30 minutes in a drying oven at 50° C.; the particles of the emulsion cream up and gather below the cover slide without undergoing coagulation. After the preparation had been examined under the microscope, a typical field was photographed (a water immersion lens and a magnification of 1000 being used). On the photograph about 300 droplets were counted and measured. Although this number may not be quite large enough for statistical purposes, it is adequate for our purpose.

Emulsions are generally characterised by the number of particles having a certain size. This method has its drawbacks, when the emulsions are very unevenly grained, as is the present case; it is not possible to see

* Cf. e.g., W. Clayton, *The Theory of Emulsions and Their Technical Treatment*, 3rd edition, p. 5 (1935).

how the mass of the disperse phase is distributed among particles of different size, and this is actually of greater interest. The masses change in a ratio of 1 : 1000, if the ratio of the particle sizes changes from 1 : 10. We have therefore preferred masses to numbers.* The results certainly are clearer, but they are represented less exactly; since we count statistically an insufficient number of particles, the rare appearance of specially large particles may be a serious cause of error.

Table III. (a) shows the distribution of the mass of particles (per cent. of total volume of disperse phase) among the particles of different size (diameter in μ).

TABLE III.—DEGREE OF DISPERSION.

Energy in Milliamps	Time of Irradiation in Minutes.	Relative Masses of Disperse Phase in Per Cent.					
		Diameter of Particles					
		0 μ -2 μ .	2 μ -4 μ .	4 μ -6 μ .	6 μ -8 μ .	8 μ -10 μ .	10 μ -12 μ .
(a) Toluene—Water—Emulsions.							
50	3	2.3	28	36	34	0	0
50	15	2.3	28	47	23	0	0
80	$\frac{1}{2}$	5.5	30	21	20	24	0
80	3	1.5	25	29	20	25	0
115	$\frac{1}{2}$	2.3	29	28	33	7.7	0
115	3	2.8	24	25	22	26	0
(b) Toluene/Sodium Oleate—Solution.							
50	3	9.6	68	16	5.7	0	—
50	15	4.8	33	37	25	0	—
80	$\frac{1}{2}$	16	45	38	0	0	—
80	3	3.7	56	40	0	0	—
115	$\frac{1}{2}$	5.8	36	29	25	3.8	—
(c) Emulsion of Toluene/Sodium Oleate—Solution, Dispersed by Steam							
Disperse Phase in Vol. Per Cent.							
12.3		2.8	16	18	16	19	28

Highly dispersed emulsions are formed, when the time of radiation is short and the energy small; under these conditions the concentration is low (cf. Table II. (a)), hence the tendency to coagulate is small. A long time of irradiation and a high energy favour coarser particles.

Dispersion becomes much more effective if an emulsifier is added (Table II. (b)). Experiments were performed under the same conditions with toluene and an aqueous solution of sodium oleate (1 per cent.). Since a slight excess of alkali favours the emulsifying action of a pure soap solution, the aqueous solution was prepared by adding somewhat more than the equivalent amount of NaOH to pure oleic acid.

The concentration of the emulsion increases with increasing time of irradiation, approaching the maximum value of 50 per cent. first rapidly, then more and more slowly. With an energy of 115 milliamps (and higher

* The particles were counted and their masses calculated in the following way: the numbers counted referred to particles with a diameter below 1 μ , between 1 and 2 μ , between 2 and 3 μ , etc. When calculating the masses the average diameter of 1.5 μ was taken for the particles between 1 and 2 μ , 2.5 μ for those between 2 and 3, etc. To simplify the tables the relative masses of two neighbouring classes as to size were united. Sizes not mentioned in the tables were not observed.

values) toluene is emulsified in an equal volume of soap solution in less than 30 seconds. If more toluene is gradually added, it is also rapidly dispersed, until a concentration of about 75 per cent. is reached. On adding still more toluene, the emulsion breaks: a thick layer of hydrocarbon appears on the top of the aqueous phase. It is rather surprising that the limiting value reached in this way agrees so well with the maximum concentration, 74.04 per cent. calculated from Wa. Ostwald's¹⁰ phase volume theory, although the premises of this theory are not fulfilled, the particles being neither of equal size nor undeformable.

A comparison of Tables III. (a) and (b) shows that the emulsifier favours a higher degree of dispersion: a very distinct maximum is found for particles with diameters between 2 and 4 μ ; 95-100 per cent. of all are below 9 μ . Evidently ultrasonics emulsify very efficiently; with simple emulsifying devices so finely grained emulsions could not be produced. It is of no avail to continue irradiating an emulsion already formed; the particles merely become somewhat coarser. Table III. (b) shows that this is also the case with stabilised emulsions. This seems to prove that the presence of stabilisers does not prevent these emulsions becoming coagulated by ultrasonics, whereas the protection by sodium oleate is so strong that the mere increase in concentration would not cause the droplets to unite.

TABLE IV.—TOLUENE—WATER—EMULSIONS. THE INFLUENCE OF THE AIR PRESSURE. TIME OF IRRADIATION $\frac{1}{2}$ MINUTE; ENERGY 115 MILLIAMPS.*

Air Pressure in mm. Hg.	Disperse Phase in Vol. per Cent.	Relative Masses of Disperse Phase in per Cent.						
		Diameter of Particles						
		0 μ -2 μ .	2 μ -4 μ .	4 μ -6 μ .	6 μ -8 μ .	8 μ -10 μ .	10 μ -15 μ .	15 μ -20 μ .
200	2.6	1.6	12	25	16	19	27	0
760	4.4	3.3	23	24	21	21	7.9	0
1100	5.0	3.0	19	22	21	18	18	0
1500	5.7	0.6	9.3	16	13	19	16	26
2300	4.1	2.7	23	33	23	18	0	0
4000	1.2	4.9	37	27	32	0	0	0

* Different glasses have been used as in the other experiments.

When discussing the mechanism of emulsification in a previous paper,¹ the influence of pressure was proved to be characteristic. Table IV. records the distribution of particle sizes for the samples irradiated at different pressures, the liquids being saturated with gas; the concentrations were as before.¹ The time of irradiation was 30 seconds, the energy 115 milliamps; 5 c.c. of toluene plus 5 c.c. of water were used; the test tube had a width of 2.5 cm. Stabilised systems could not be investigated in this way because spontaneous emulsification occurred, whilst the liquids were saturated with the gas.

The degree of dispersion shows two minima: one at very low pressures, one at about 2 atmospheres. This rather complicated behaviour may probably be explained when considering the mechanism of emulsification and the fact that in the same system both high concentration and coarse particles are usually favoured by similar conditions.

The emulsification of oils by cavitations produced by other means (*cf.* previous paper, p. 838), *i.e.*, by the collapse of steam bubbles, was also investigated as to degree of dispersion. An emulsion, prepared in this manner, stabilised by sodium oleate, was investigated as to particle distribution (*cf.* Table III. (c)).

¹⁰ Wa. Ostwald, *Koll. Z.*, 1910, 6, 103; 1910, 7, 64; 1929, 47, 131.

This result may be compared with the first experiment in Table III. (b) (50 milliamps, time of radiation 3 minutes; cf. also Table II. (b)). With ultrasonics the maximum is obviously more distinct; the emulsion is more evenly, and also more finely grained.

2. Metal Emulsions.

Mercury and "oils" differ as to their mechanism of emulsification (cf. the two previous papers¹). This difference is probably due to the high interfacial tension of mercury. Since fused metals also have high interfacial tensions, we may expect them quite generally to be emulsified by the same mechanism. This was confirmed with Wood's metal, tin, sodium and potassium.

Concentrated emulsions in aqueous and non-aqueous liquids may be prepared with *Wood's metal*. The regulus of the metal, solidified during irradiation, always contained marked amounts of enclosed liquid,² and its surface was covered with a large number of blisters. This is clear proof that dispersion is actually caused by the bursting of metal films covering

TABLE V.—CONCENTRATIONS.

Energy in Milliamps.	Disperse Phase in g/l.								
	Time of Irradiation in Minutes								
	½.	1.	1.	2.	3.	5.	10.	15.	30.
(a) Emulsions of Hg in Sodium Citrate—Solution.									
70	—	—	2.2	—	4.6	6.2	6.3	6.1	—
100	4.0	6.3	5.2	6.4	—	5.5	6.4	—	—
130	—	—	6.3	—	5.5	—	—	—	—
(b) Emulsions of Hg in Lysalbinic Acid—Solution Concentrations.									
60	—	—	1.1	7.5	—	16	—	12	12
100	6.4	10	11	—	—	23	—	63	—
130	15	19	57	—	—	57	—	53	—

bubbles of the dispersion medium. Very finely grained emulsions are produced in bromo-naphthalene and tetrachloro-ethane; they contain a large amount of particles of colloidal size; when the coarser particles have settled, the fluid above them is a stable, brown colloidal solution. Under the ultramicroscope strongly scintillating particles are visible, as is frequently the case with colloidal metal solutions.

The *alkali metals* form concentrated emulsions in organic liquids such as paraffin oil and xylene. Those in paraffin oil have very intense colours: reddish violet in the case of sodium, bluish green in that of potassium (owing to oxidation these colours disappear in course of time).

Mercury is the most suitable metal for quantitative experiments, since it is easily purified, and is chemically fairly inert. Table V. (a) records the concentrations found with 0.5 c.c. of distilled mercury in 5 c.c. of 0.002 mol. sodium citrate solution.¹¹

The limiting concentration is about 6 g. per litre; its absolute value is practically independent of the energy introduced, but the rate with which it is reached increases with increasing energy. With somewhat smaller energy (50 or 60 milliamps) the rate of emulsification is so low that no equilibrium can be reached within a reasonable time.

¹¹ H. B. Bull and K. Söllner, *loc. cit.*²

In order to determine the degree of dispersion the emulsion, just formed, was stabilised with lysalbinic acid and glycerol was added to minimise the Brownian movement, and was then photographed, after having sedimented entirely (Table VI. (a)).

These emulsions are more finely grained than oil emulsions, but the droplets sediment fairly rapidly owing to the high density of mercury. With increasing energy and time of irradiation they become coarser, even when the concentration remains unchanged.

Similar experiments were performed with solutions containing an emulsifier; the mercury was dispersed in a 0.05 per cent. solution of lysalbinic acid, a substance well known as a powerful stabiliser for metals. Tables 5(b) and 6(b).

It is rather surprising that the drops of the stabilised emulsion are distinctly coarser than those of the pure ones. This is probably due to the

TABLE VI.—DEGREE OF DISPERSION.

Energy in Milliamps.	Time of Irradiation in Minutes.	Relative Masses of Disperse Phase in per Cent.						
		Diameter of Particles						
		0μ-1μ.	1μ-2μ.	2μ-3μ.	3μ-4μ.	4μ-5μ.	5μ-6μ.	6μ-7μ.
(a) Emulsions of Hg in Sodium Citrate—Solution								
60	15	1.2	32	26	41	0	0	—
70	1½	3.5	37	40	20	0	0	—
70	5	1.8	31	30	25	13	0	—
100	½	1.1	34	31	20	14	0	—
100	2	0.6	26	34	17	19	0	—
(b) Emulsions of Hg in Lysalbinic Acid—Solution								
60	15	1.5	29	52	21	0	0	0
70	1	0.8	11	31	13	27	18	0
70	5	0.3	0.1	23	30	31	9.4	0
100	½	0.6	14	27	21	16	22	0
100	2	0.3	7.4	13	11	28	31	0
130	2	0.2	5.2	14	18	23	39	0

following facts: large drops, if formed at all, are stabilised by the emulsifier, and are therefore more likely to survive in stabilised emulsions; in pure emulsions they have a stronger tendency to disappear, coalescing with the bulk of the mercury. This easily happens, for the majority of metal films break in the interior of the mercury,¹¹ when bubbles of the non-metallic solution are driven together; the drops are there very close to the bulk of the metal. Large drops are formed, when thick films disrupt.¹² So long as the external vibrational energy is small such thick films become spontaneously thinner, and only disrupt owing to the action of the interfacial tension. If, however, the vibrational energy is large, it will cause the disruption of thicker films. The stabiliser may also favour thicker films: the rate at which these become thinner will be smaller when the mercury moves between the two films of adsorbed stabiliser; the life of the thick film is longer, and hence it is more probable that it will be dispersed by the high vibrational energy.

¹¹ On theoretical grounds, N. Marinesco has also come to the conclusion that ultrasonics of high energy produce coarser emulsions than vibrations of lower energy. But as we are unable to agree with his assumptions on the mechanism of the formation of these metal films, we prefer not to discuss his calculations on the relationship of particle size and energy.

Here the Hg is always covered with a thick grey sediment, which grows with increasing time of irradiation. Although these stabilised emulsions settle out and become somewhat coarser in time, they are very stable, and may be readily redispersed by gentle shaking, even after several weeks. The non-stabilised emulsions of Hg in water coalesce much more quickly; after several hours the amount still dispersed is distinctly less, and after 24 hours only a small fraction of the dispersed Hg has failed to unite with the metal in bulk.

We compared the emulsification of *mercury* in a number of *organic liquids*. In all cases 0.5 c.c. of mercury and 5 c.c. of liquid were irradiated with 115 milliamps for 1 minute. The concentration determined under these conditions is generally already the limiting value found for sodium

TABLE VII. EMULSIONS OF Hg IN ORGANIC LIQUIDS. CONCENTRATIONS AND DEGREE OF DISPERSION. ENERGY 115 MILLIAMPS. TIME OF IRRADIATION 1 MINUTE.

Medium of Dispersion.	Disperse Phase in g. l.	Relative Masses of Particles in Per Cent.							
		Diameter of Particles.							
		0 μ -1 μ .	1 μ -2 μ .	2 μ -3 μ .	3 μ -4 μ .	4 μ -5 μ .	5 μ -10 μ .	10 μ -7 μ .	7 μ -5 μ .
Methyl alcohol	2.0	—	—	—	—	—	—	—	—
Ethyl alcohol	4.7	—	—	—	—	—	—	—	—
n-Propyl alcohol	8.4	1.0	2.4	3.4	2.8	1.3	0	0	0
iso-Propyl alcohol	11.2	—	—	—	—	—	—	—	—
n-Butyl alcohol	8.7	0.6	1.3	2.5	1.0	2.4	2.1	0.5	0
iso-Butyl alcohol	12.1	—	—	—	—	—	—	—	—
iso-Amyl alcohol	17.9	1.0	5.6	1.0	1.7	1.1	1.3	4.5	0
Ethyl acetate	1.0	—	—	—	—	—	—	—	—
Chloroform	1.2	1.4	3.4	4.9	1.6	0	0	0	0
Chloroform (cooled with CO ₂ -Ether)	3.2	1.0	3.8	2.0	1.8	1.3	0	0	0
Nitrobenzene	7.5	0.7	1.6	4.2	2.6	1.6	0	0	0
Nitrobenzene (with rubber)	17.3	0.3	3.8	1.2	8	8.4	1.5	1.3	4.0
Petroleum ether (with rubber)	—	0.7	9.5	1.5	1.6	2.7	1.2	2.0	0
Ethylene glycol	7.6	0.7	9.2	1.2	1.1	1.2	2.1	3.5	0
Glycerin *	8.3	1.2	1.8	2.1	1.0	7.3	—	4.3	0
Benzyl alcohol	12.2	0.9	1.1	1.1	7.0	1.1	1.4	4.5	0
Paraffin oil	—	1.1	1.3	1.4	1.4	1.0	1.8	3.1	0
n-Butyl chloride	0.4	—	—	—	—	—	—	—	—
Ethyl bromide	12.3	—	—	—	—	—	—	—	—

* No saturation was obtained after 1 minute irradiation.

citrate solution (*cf.* Table VIII.) and also for non-aqueous liquids, provided that their viscosity was not too high. In order to microphotograph and thus determine the degree of dispersion, the emulsions were mixed with viscous paraffin containing a small amount of rubber.

We make no mention of several liquids, because the concentration was too small to be determined: cyclo-hexane, petroleum ether, benzene, toluene, xylene, ether, acetone, chlorobenzene, carbon disulphide. These liquids also, however, can form unstable and not very concentrated emulsions, if exposed to ultrasonics at a temperature close to the melting point of mercury.

With viscous liquids, such as glycol, glycerol, benzyl alcohol, very concentrated emulsions are produced. In this respect, mercury differs markedly from the "oils." As regards the latter, a high viscosity of the

aqueous phase is most disadvantageous for emulsification (Table VIII.). The amount dispersed was only estimated approximately from the aspect of the emulsion, a method which, as mentioned above, has been proved to be

TABLE VIII.—THE INFLUENCE OF THE VISCOSITY ON THE EMULSIFICATION OF BENZENE AND Hg.

Medium of Dispersion.	Viscosity of the Medium of Dispersion 1000 η (20°).	Turbidity of the Emulsion.	
		Disperse Phase	
		Benzene.	Hg.
Water	10	++++	+++
Cane-sugar solution 10 per cent.	13	++++	++++
" " 20 " . . .	19	++++	++++
" " 30 " . . .	—	+++	++++
" " 40 " . . .	60	+++	+++++
" " 50 " . . .	—	++	+++++
" " 60 " . . .	565	----	+++++
Ethylene glycol	173	+	++++
Glycerin	14000	----	++++

sufficiently trustworthy. Benzene serves as an example for all other organic liquids.

This dissimilarity shows again the distinction which is to be drawn with regard to the mechanism of emulsification: high viscosity tends to prevent the formation of cavities, and the consequent strong mechanical

TABLE IX.—INFLUENCE OF AIR UPON THE EMULSIFICATION OF Hg. ENERGY 115 MILLIAMPS. TIME OF IRRADIATION 2 MINUTES.

Medium of Dispersion.	Disperse Phase in g. l.	Relative Masses of Disperse Phase in Per Cent.							
		Diameter of Particles							
		0.4-1.0	1.0-2.0	2.0-3.0	3.0-4.0	4.0-5.0	5.0-6.0	6.0-7.0	7.0-8.0
Distilled H ₂ O *	4.3	1.7	28	22	20	28	0	0	0
Distilled H ₂ O boiled *	0.7†	3.0	39	24	23	11	0	0	0
Sodium-citrate solution (boiled) *	1.3	2.4	27	39	31	0	0	0	0
Solution of lysalbinic acid (boiled) *	16.5	0.6	16	26	12	26	20	0	0
n-Butyl alcohol (in vacuo) ‡	6.2	0.2	2.1	4.6	11	20	12	20	31
Nitrobenzene (in vacuo) ‡	6.5	0.5	10	20	20	14	14	22	0

* 0.5 c.c. Hg and 25 c.c. of liquid were radiated in tubes of 25 mm. diameter.

† With carefully degassed water the emulsions are still less concentrated.

‡ 0.5 c.c. Hg and 5 c.c. of liquid were radiated in the usual tubes.

effects when the cavities, if formed, collapse; hence oils are but feebly dispersed in highly viscous liquids, so long as they do not show a strong protecting action. In the case of mercury a high viscosity of the other

phase does not seriously interfere with the formation of thin mercury films and their disruption. Thus small drops of mercury may readily be produced and high viscosity favours the stability of the emulsion formed.

In the homologous series of the aliphatic alcohols the stability of the emulsion increases, when ascending the series. To a certain extent, the change observed when passing from one alcohol to the next recalls the variation known as Traube's rule. The distinctly stronger emulsification in bromine derivatives when compared with closely related chlorine compounds is remarkable: ethyl bromide producing a concentrated emulsion, butyl chloride a very poor one. A similar difference exists between bromo- and chloro-benzene. Probably some surface reaction in the case of the bromo-substituted compounds is the reason for this behaviour.

Table VII. shows further that—as in the case of stabilised and non-stabilised aqueous mercury emulsions—a high limiting concentration may frequently coincide with a low degree of dispersion.

In previous experiments it had been observed that these unprotected emulsions are in many cases markedly stabilised by gases. Some determinations of the limiting concentration and the degree of dispersion are shown in Table IX.

In aqueous emulsions the influence of air is very distinct: in absence of air the limiting value is much smaller, both in pure water and in citrate

TABLE X.—CHANGE OF CONCENTRATION OF Hg-EMULSIONS IN COURSE OF TIME. ENERGY 115 MILLIAMPS. TIME OF IRRADIATION.

Time after Emulsification.	Disperse Phase in g./l.			
	In Nitrobenzene.		In <i>n</i> -Butylalcohol.	
	+ Air.	In Vacuo.	+ Air.	in Vacuo.
1 minute .	8.4	6.4	7.6	6.0
30 minutes .	6.4	1.6	3.5	1.2
3 hours .	5.0	1.3	2.4	1.5
16 hours .	4.1	0.9	2.0	Nearly clear.
48 hours .	3.0	Nearly clear.	1.6	Clear.

solution. A stabiliser such as lysalbinic acid is, of course, more powerful than air. Again, the more stable emulsions are coarser. The influence of air does not at once appear so distinctly in organic liquids. The limiting value shortly after irradiation is not so much changed. The difference becomes more obvious in course of time, the drops in the air-free emulsion coalescing more quickly than in those containing air. Owing, probably, to this rapid coalescence, the air-free emulsions seem to be coarser (Table IX.).

Table X. also indicates quite generally the degree of stability of Hg-emulsions in organic liquids. In solvents with a higher emulsifying power and higher viscosity, the emulsions (although settling down) are usually somewhat stable; in liquids like methyl- or ethyl-alcohol the particles unite in the course of several hours with the Hg in bulk.

In the presence of rubber as a stabilising agent very concentrated and stable emulsions may be obtained in many organic liquids.

Summary.

1. The concentration and the degree of dispersion were determined in emulsions produced by ultrasonic waves under different conditions of time and energy of irradiation; the investigation was extended to emulsions of

organic liquids in water and *vice versa*, and of mercury in water and organic liquids, both in the presence and in the absence of an emulsifying agent.

Our heartiest thanks are due to Professor H. Freundlich for his interest in this work. We are also greatly indebted to Professor F. G. Donnan, F.R.S., for his generous hospitality.

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NOTE ON THE DECOMPOSITION OF NITROGEN IODIDE.

BY W. E. GARNER AND W. E. LATCHER.

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The composition of nitrogen iodide, when prepared by the addition of iodine to concentrated ammonia solution,¹ is very probably $\text{NI}_3 \cdot \text{NH}_3$. According to these authors, it decomposes giving nitrogen, iodine, and ammonium iodide as products in the proportions given by the equation $8\text{NH}_3\text{NI}_3 = 5\text{N}_2 + 6\text{NH}_4\text{I} + 9\text{I}_2$, and Eggert has shown that it gives the same products whether it is decomposed in the dark, or under the action of light or by detonation. The dark reaction proceeds at a measurable rate at room temperature, 80 per cent. being decomposed in 24 hours. The substance appeared to be promising for investigations into the relationship between thermal decomposition and detonation, similar to those previously carried out on lead azide, lead styphnate, and mercury fulminate, in which cases measurements were made of the change in length of induction period with temperature, and the rate of the thermal decomposition immediately preceding detonation.²

Eggert states that it is possible to dry $\text{NH}_3 \cdot \text{NI}_3$ in a cathode vacuum without appreciable loss of weight, but this we have found to be impossible with an iodide prepared by running 880 ammonia into iodine in potassium iodide. The dry iodide always detonated after a few minutes at pressures below 2×10^{-3} cm. at the temperatures -20° — 20°C . The detonation apparently occurred as soon as the solid became dry. This made it impossible to proceed with the measurement of induction periods but the occurrence of detonation under such conditions was a phenomenon which was in itself of sufficient interest to warrant investigation.

Experimental.

Nitrogen iodide was made by running 10 c.c. of 880 ammonia into a few c.c. of 0.07 molar I_2 in normal KI solution and the precipitate washed

¹ Chattaway and Orton, *Amer. Chem. J.* 1900, 24, 159; Eggert, *Z. Elektrochem.*, 1921, 27, 547.

² Garner and Gomm, *J.C.S.*, 1931, 2123; Garner and Hailes, *Proc. Roy. Soc.* 1933, 139A, 576; Hailes, *Trans. Faraday Soc.*, 1933, 29, 342.

free from potassium iodide with N/100 ammonium hydroxide. Usually 0.01 to 0.025 grams of nitrogen iodide were prepared at a time. The precipitate was transferred to a small glass filtering funnel containing a pad of asbestos at the bottom and the bulk of the water removed by suction with a water pump. The funnel containing the iodine was lowered into a pyrex bulb, 5.5 cm. in diameter and 10 cm. long by the spindle device (Garner and Gomm),² and the bulb evacuated through a carbon dioxide trap by means of a Hyvac and a mercury vapour pump. Phosphorus pentoxide was usually placed at the bottom of the bulb, to assist in the drying process. Detonation always occurred during the evacuation at pressures of the order of 10^{-4} cm. On account of the well-known sensitivity of nitrogen iodide to a blow, the detonation might have been caused by the fall of small crystals from the side of the glass funnel on to the crystals below, so that it was necessary to eliminate this possibility. After washing the iodide on a filter paper, it was transferred on a spatula to a very flat bucket made of either glass or platinum and introduced into the reaction vessel in this form. The chance of falling particles was thereby

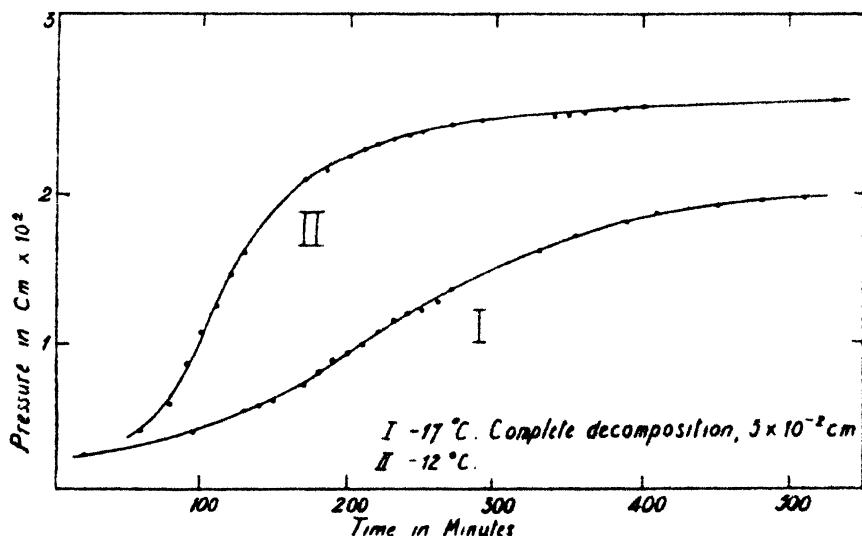


FIG. 1.

much reduced, but nevertheless detonation always occurred in a hard vacuum after an interval of time which varies with the temperature of the iodide. At 20° C. it was 25 minutes, at 10° C. 50 minutes, and at 1° C. 60 minutes. It was noted that detonation occurred at about the time when the solid became dry.

It was found possible to dry the iodide if the removal of water was carried out at pressures not lower than 2×10^{-3} cm., and having dried it in this way, to study the mode of its thermal decomposition. Approximately 0.01 gm. of iodide (slightly moist) was placed in a flat platinum bucket and dried over a layer of P_2O_5 at a pressure of 2×10^{-3} cm., and the rate of evolution of nitrogen was measured on a McLeod gauge. Typical curves are given in Fig. 1 for experiments at -17° and -11° C. respectively. There was a quiescent period during which the increases of pressure were small and irregular, which was probably due to slight decomposition occurring while the solid was drying. After this period, the rate of evolution of gas accelerated, then became approximately constant for a time, and finally slowed down practically to a standstill, although a large fraction of the iodide was still intact.

During the reaction, the walls of the vessel gradually became browned by the products. The deposit was transferred to the trap and on analysis was shown to be mainly iodine, and contained but a trace of ammonia. The reaction was thus occurring in an atmosphere of iodine vapour which increases in density with time, and it was possible that the retardation of the reaction was due to this cause. To test this, the pressure was reduced to 2×10^{-3} cm., and after a few minutes which sufficed to remove the iodine, the decomposition began afresh. As before, the reaction again slows down after a time and can be accelerated again by the removal of the products from the reaction bulb. Usually 0.01 gm. iodide can be completely decomposed after two evacuations of the products. On the other hand, if the pressure was reduced below 2×10^{-3} cm., the residual iodide detonates after the lapse of a few minutes, just as it did during the drying process if the pressure fell too low.

The length of the quiescent period was irregular and probably depended on the amount of water present in the iodide at the beginning of the experiment. Also the pressure-time curves were not reproducible at any one temperature, so that quantitative investigation of the phenomena will prove a difficult matter.

It was noted that the total nitrogen liberated was always 40-60 per cent. lower if detonation occurred at the commencement of the reaction than for decomposition without detonation. Similar phenomena are usually observed when small amounts of explosive are detonated in vacuum, and are due probably to the scattering of small particles of solid.

Conclusions.

Nitrogen iodide can be completely decomposed at -20°C . and upwards without detonation occurring, if the pressure above the solid be kept above 2×10^{-3} cm. Under these conditions, the volatile products of the reaction accumulate around the solid and this prevents the reaction getting out of hand. The reaction may be brought practically to a standstill if the vapour pressure of the products becomes sufficiently high. Water also confers a certain measure of stability on nitrogen iodide.

In a hard vacuum, however, the water and the products of the reaction are so rapidly removed from the neighbourhood of the solid, that the reaction gets out of hand and detonation occurs.

The decomposition of nitrogen iodide has many of the features of a chain reaction and the above phenomena can be explained on this basis. In the absence of adsorbed water vapour or iodine, these chains have probably an infinite length, thus accounting for detonation. Iodine or water molecules adsorbed on the crystal surfaces are able to break the chains and so reduce the rate of reaction to measurable dimensions. This case is of interest because in the solid reactions hitherto investigated, reaction occurs more readily in the interface between the solid and its products than on the bare solid surface, whereas the reverse is true for nitrogen iodide. It is thus an example of a negative catalytic effect caused by the products. The instability of crystals of nitrogen iodide when the surfaces are free from adsorbed water or iodine probably accounts for its high sensitivity to shock, for fracture of the crystals produces momentarily surfaces free from adsorbed gases, and under such conditions it has been shown that the crystals detonate.

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THE BEHAVIOUR OF WATER HELD IN FINE-PORED MEDIA.

A Correction

BY B. H. WILSDON, D. G. R. BONNELL AND MISS M. E. NOTTAGE.

Received 17th January, 1936.

We are indebted to Dr. R. K. Schofield of the Rothamsted Experimental Station for pointing out certain errors in our paper appearing under the above title.¹ These involve the indirect calculations of hydrostatic pressure from the published data of other workers plotted in Fig. 3.

In a recent paper,² Schofield uses the equation $\Delta P_{\text{atm.}} = 0.09\Delta T$ to calculate the hydrostatic pressure to which a liquid held in a porous medium is subjected from the lowering of the freezing-point ΔT . In the derivation of this relationship, it appears to be assumed that, on freezing, the ice separates at atmospheric pressure. The results of Bouyoucos and Parker quoted by us were calculated according to the formula

$$\frac{dp}{dT} = \frac{L}{T(v_1 - v_2)},$$

where L is the latent heat of fusion and v_1 and v_2 the specific volumes of water and ice respectively, on the assumption that the ice must be regarded as separating under the hydrostatic pressure of the liquid. This gives, however, a result of the opposite sign to that plotted by us. We find it difficult to accept Schofield's calculation, in which the volume change of the phases is ignored, for the reason that a positive pressure will usually be exerted by the ice on freezing. It must be admitted, however, that no alternative calculation which can take account of this condition is yet available.

Two other inaccuracies have also been detected: (i) In the curve derived from Szigeti's vapour pressure data the water content should be regarded as too high by 9.2 per cent. (ii) Owing to some ambiguity in Thomas's paper as to the actual temperature of experiment, and the corresponding true values of the vapour pressure of pure water, the derived values of the hydrostatic pressure at the highest water content should be 2.5 atmosphere; the values at lower water contents are only slightly affected.

The corrected data still show discrepancies and, although we realise that no strict comparisons can be made between the materials to which these calculations apply and those used in our own experiments they tend, in our opinion, to reinforce the direct evidence obtained by us for the existence of an anomaly in the behaviour of liquids in porous media, and emphasise the desirability of obtaining measurements for the free energy of liquids in porous media by independent methods, as pointed out by us in our original communication.³

¹ *Faraday Soc. Trans.*, 1935, **31**, 1304.

² *Trans. 3rd Int. Cong. Soil Science*, Vol. II., 37, 1935.

³ *Nature*, 1935, **135**, 186.

THE PHOTODECOMPOSITION OF IODOFORM AND OF THE ALKYL AND ALKYLENE IODIDES.

By K. E. GIBSON AND T. IREDALE.

Received 1st April, 1935.

Organic compounds containing iodine are, generally speaking, unstable in the presence of light, whether oxygen be dissolved in them or not.^{1, 2} Iodine is the most obvious product of decomposition, and is accompanied by hydrocarbons, which are the results of secondary reactions. It is considered that the carbon-iodine linkage is affected by the absorbed light, the excited state which arises is thought to involve a repulsion between the two atoms similar to the case of hydrogen iodide.^{3, 4} The absorption spectra of most of the gaseous alkyl iodides are continuous in the near ultra-violet region, and so also are the spectra of gaseous methylene iodide and iodoform.⁵ One would expect the quantum efficiency for the decomposition of these substances to be at least unity. An approximation to this was found by one of us working with liquid ethyl iodide.² Later W. N. Wallace found a very small, almost immeasurable, quantum efficiency for the decomposition of gaseous methyl iodide. This result was not published, but others have recently confirmed it.⁶ Work on these substances was continued, with interruptions, until the present time. We present some results we have obtained with iodides of the simpler type, especially iodoform, which has usually been submitted to a photochemical oxidation.^{7, 8} No quantum efficiency for the simple decomposition process seems to have been determined.

Experimental.

The source of radiation was a Hanovia mercury vapour lamp, working on the 240 A.C. 50 cycle circuit, with the aid of a step-down transformer. The output was remarkably steady, only very occasional fluctuations in intensity were observed. By means of an aperture in front of the lamp, quartz lenses, and a large screen with the necessary opening, an approximately parallel beam of light was obtained, which could be focussed to fit exactly the circular opening in front of the thermopile elements. The thermopile was a Moll, large surface type, used without any cover, and fitted with a rubber ring, blackened on the outside. The internal diameter of this ring was the same as the diameter of the opening in front of the thermoelements. The thermopile and photochemical cell were mounted on a board in front of the screen, permitting easy alignment and forward and lateral movements of the thermopile. A Moll galvanometer was employed in conjunction with the thermopile.

¹ Job and Emschwiller, *Compt. Rend.*, 1924, **179**, 52.

² Iredale, *J. Physic. Chem.*, 1929, **33**, 290.

³ Herzberg and Scheibe, *Z. physik. Chem.*, 1930, **7B**, 390.

⁴ Iredale and Mills, *Proc. Roy. Soc.*, 1931, **133A**, 430.

⁵ Iredale and Stobo, *Z. physik. Chem.*, 1933, **20B**, 340.

⁶ Bates and Spence, *J. Amer. Chem. Soc.*, 1931, **53**, 1089.

⁷ Plotnikow, *Z. physik. Chem.*, 1911, **75**, 396.

⁸ Mukherji and Dhar, *J. physic. Chem.*, 1931, **35**, 1790.

Calibration.—The thermopile was calibrated with the aid of a Hefner lamp, certified by the Reichanstalt. We followed the method of Coblenz,⁹ using a 40 mm. aperture, the whole operation being carried out in a blackened cupboard with a movable blackened screen between lamp and thermopile. Draughts were eliminated as much as possible. Instead of using variable heights of flame and plotting a curve as Coblenz suggests, we worked with a fixed height (40 mm.), and carried out a large number (over 70) separate measurements, using the mean of these results in all subsequent calculations. Using Coblenz's figure for the Hefner lamp (23×10^{-6} gram-calories per sq. cm. per sec.) this came out to be 3.42×10^{-6} gram-calories per sq. cm. per sec. for 1 cm. deflection on the galvanometer scale 1 metre from the galvanometer. Pure re-distilled amyl acetate (Kahlbaum) was used in the Hefner lamp, but no correction was applied for carbon dioxide and water vapour in the atmosphere, as this correction seems a little uncertain. At the conclusion of our measurements we checked our procedure with the aid of the uranyl oxalate actinometer described by Leighton and Forbes.¹⁰ With the stirred solution and radiation of wave-length 3130 Å., we obtained, at 15° C. a quantum efficiency of 0.568 for the oxalate decomposition, which agrees very well with Leighton and Forbes's figure.

Filters.—For light of wave-length 3650 and 3660 Å. in the mercury arc we used Winther's rosaniline hydrochloride (0.03 per cent.) filter, and for 3130 Å., Winther's filter containing potassium chromate and nitrosodimethylaniline. This latter filter admits a little 3020 Å. light, but the intensity of this is less than the 3130 intensity in the mercury arc, and no great error is incurred through taking the total light absorbed as having a wave-length of 3130 Å. Infra-red radiation was shut off (partly) by means of water filters.

Photochemical Cell.—This was about 5 cm. long, with plane quartz ends. A weighed quantity of the substance was introduced into it, and the solvent dissolved over in a current of carbon dioxide. Caps were then fitted, and the contents sealed. In certain cases, *e.g.*, iodoform, the distillation was carried out in the dark.

Solvents.—Owing to the low vapour pressure of many of these iodides, investigations of their photodecomposition had to be carried out in solution, in order to obtain sufficient concentration. Benzene was the principal solvent, but we also used ethyl alcohol. The objections to this latter solvent will be discussed later.

Method.—The difference in the galvanometer deflections for the light beam falling on the thermopile when the photo-cell contained only the solvent and when it contained the solution, was taken as a measure of the absorbed light energy. (A correction should be applied in a more round-about way for the amount of light reflected and absorbed by the quartz end plates, and many investigators have worked out formulæ for this correction, sometimes introducing assumptions as to the magnitude of certain absorption coefficients, etc., which were never properly verified. We do not think that its omission will sensibly affect our main considerations, because we checked our results with the aid of the uranyl oxalate actinometer.)

The decomposition was never allowed to proceed so far as to involve appreciable absorption of the light by the liberated iodine. The galvanometer deflections were carefully checked at the beginning and end of the decomposition. The liberated iodine was titrated with a very dilute solution of sodium thiosulphate, a similar amount of the undecomposed solution being used as a comparison. This method is quite accurate, because it can be checked against solutions of known iodine content. In some cases, *e.g.*, iodoform, the titration had to be carried out with carbon

⁹ Coblenz, *Bur. Standards Bulletin*, 1914, 11, 87.

¹⁰ Leighton and Forbes, *J. Amer. Chem. Soc.*, 1930, 52, 3139.

dioxide or hydrogen bubbled through the solution, as well as through the comparison solution.

Purity of Materials.—Thiophene free benzene was dried over calcium chloride and distilled. Absolute alcohol was distilled after standing over lime.

Iso-amyl iodide (Kahlbaum) was shaken with dilute sodium thiosulphate to remove traces of iodine, washed with water, dried over anhydrous sodium sulphate, and several times distilled, finally under reduced pressure, and kept in a dark bottle over silver foil. Cetyl iodide was pared by Mr. C. McGregor of the Department of Organic Chemistry, and was re-crystallised from ethyl alcohol. The material was pure white, with no trace of decomposition. Methylene iodide was made from iodoform and sodium arsenite,¹¹ re-crystallised several times, and distilled under reduced pressure. The final product had still a faint yellow colour, probably due to traces of iodoform, but the light absorption due to this in dilute solution was negligible. Iodoform was obtained from a good commercial sample by re-crystallisation several times from alcohol, and had a sharp melting-point (120°). Tertiary-butyl iodide was made from tertiary butyl alcohol and constant boiling-point hydriodic acid.¹² The distillate was shaken with dilute sodium thiosulphate, water, dried, and distilled under reduced pressure. The iodide remained colourless if kept unexposed to light and air.

Discussion.

The quantum yield in the photodecomposition of iodoform in benzene in the absence of oxygen appears to be unity, if the results in Table I. are to be accepted as reliable. The region 3650 \AA. occurs in the first absorption band (continuous) of iodoform, and 3130 \AA. in the second.

TABLE I.

Conc. in Moles per Litre.	Time of Irradiation. (Hrs.) (Mins.)	Quanta Absorbed. ($\times 10^{19}$).	Atoms of I. ($\times 10^{19}$).	Quantum Yield.	Wave-Length \AA.	Temp. $^{\circ}\text{C.}$
Iodoform in Benzene.						
0.0282	5 18	14.70	14.75	1.01	3130	19.0
0.0282	4 41	13.00	13.70	1.05	3130	18.5
0.0282	3 42	10.00	10.00	1.00	3130	18.0
0.0282	4 54	14.00	14.50	1.04	3130	18.0
0.0282	4 0	11.50	12.10	1.05	3130	22.0
0.0028	3 0	8.70	9.45	1.09	3130	21.0
			Mean	1.04		
0.0282	7 21	2.35	2.21	0.94	3650	25.0
0.0282	6 21	2.03	1.85	0.91	3650	24.0
0.0028	5 55	1.90	1.69	0.89	3650	24.0
			Mean	0.91		
Iodoform in Ethyl Alcohol.						
0.0282	6 45	2.96	3.01	1.01	3650	16.5
0.0282	9 30	4.05	4.05	1.00	3650	17.0
0.0141	6 45	2.78	3.00	1.04	3650	17.0
			Mean	1.02		
0.0282	6 19	3.50	5.75	1.61	3130	18.0
0.0282	5 57	3.31	5.45	1.64	3130	17.5
0.0282	7 24	4.40	6.92	1.57	3130	18.0
			Mean	1.61		

¹¹ *Organic Synthesis* (Adams), 1921, 1, 57.

¹² Norris, Watt and Thomas, *J. Amer. Chem. Soc.*, 1916, 38, 1071.

The two maxima in the iodoform absorption occur at about 3500 Å. and 2940 Å., a frequency difference of 5440 cm^{-1} , which is a little too small for the energy of excitation ($^3P_{-1} - ^3P_{-2}$) of the iodine atom (7600 cm^{-1}). Nevertheless, these maxima (with separations varying from 5600 to 7800 cm^{-1}) occur in the continuous absorption spectra of other polyiodides, and it is difficult to attribute them to anything else. It can certainly be accounted for by the varying slope of the potential curves for the upper, excited state, as previously shown.⁶ We can assume that CHI_3 dissociates in the first region into CHI_2 and I ($^3P_{-1}$), and in the second into CHI_2 and I ($^3P_{-2}$). The quantum yield need not be very different in the two processes, but there are more possibilities of secondary reactions in the second region, because the I atom possesses excess energy of 21,000 calories (per gram atom), and the yield may therefore increase, with decrease in wave-length of the absorbed light.

The quantum, yield of unity may be fortuitous, in that two distinct secondary effects may be operative: (i) deactivation by collision (even with unstable, "repulsion" states this is not impossible¹³); and (ii) secondary reactions of the products of decomposition. The one will tend to diminish the yield, the other, in most cases, to increase it. But if such effects are operating it is remarkable that the yield is not more greatly influenced by the concentration.¹⁴

In the presence of oxygen the quantum yield is much greater⁸ and it varies very much with the solvent employed. It seems that solvents with low dielectric constant give the highest yields,¹⁵ a state of affairs not easy to predict. The oxidation of the CHI_2 radicle evidently initiates a chain reaction involving further CHI_3 molecules, which is responsible for the photochemical after-effect.

The quantum yield in alcohol seems to be a little higher, but it is doubtful if these results are as reliable as those obtained with benzene as solvent. Iodine slowly reacts¹⁶ with ethyl alcohol with formation of HI , and this would give with the liberated iodine a certain amount of the I_3 ion. As this absorbs very strongly in the iodoform region, the apparent absorption of the light by the iodoform, as measured, may be too great. Moreover, the formation of the HI would tend to diminish the yield of iodine, so that on both accounts the apparent quantum yield should be lower than anticipated. That this is not the case points to some other factor, such as the possible reaction between HI and CHI_3 , or the influence of the solvent on the secondary reaction. Altogether, it would be safer not to base too many conclusions on the results obtained with alcohol as solvent.

The results we have obtained with the other iodides point to some variation of the quantum yield with the structure of the molecule, although it is not easy to account for these variations in any simple way. (Table II.). It seems that the quantum yield increases in the order: (a) iso-amyl \rightarrow cetyl; ¹⁷ (b) methylene \rightarrow iodoform; and (c) iso-amyl \rightarrow tert-butyl; that is, there is an increase in the quantum yield with (a) increase in length of carbon chain; (b) further replacement of hydrogen

¹³ Franck and Rabinowitsch, *Trans. Faraday Soc.*, 1934, **30**, 120.

¹⁴ West and Paul (*Trans. Faraday Soc.*, 1932, **28**, 688) found with ethyl iodide that the yield was remarkably independent of the concentration.

¹⁵ Winther, *Trans. Faraday Soc.*, 1926, **21**, 595.

¹⁶ Batley, *ibid.*, 1928, **24**, 438.

¹⁷ The results which one of us⁸ obtained with ethyl iodide cannot be included here, as the liquid itself was used, the substance acting as its own solvent, wholly different from benzene.

by halogen; and (c) change of central carbon atom from primary to tertiary. These effects run parallel with the results of Hartel and Polanyi,¹⁸ who investigated the reactivity of the sodium atom with the chlorides; the diminishing activation energies in their experiments correspond to the increasing quantum yields in ours.

Bates and Spence considered that the low quantum yield in the case of methyl iodide was due to the great stability of the CH_3 radicle, and its ready recombination with the liberated I atom, $\text{CH}_3 + \text{I} = \text{CH}_3\text{I}$. (More generally $\text{R} + \text{I} = \text{RI}$.) The increase in quantum yield as the molecule is lengthened or its hydrogen replaced by halogen, etc., must then be due to the reactions (i) $\text{R} + \text{R} = \text{RR}$ or $\text{R}' + \text{R}''$ ($\text{R}' =$ saturated hydrocarbon, $\text{R}'' =$ unsaturated (olefine) hydrocarbon), and (ii)

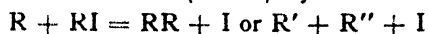


TABLE II.—WAVE-LENGTH = 3130 Å.

Iodide in Benzene.	Conc. in Moles per Litre.	Time of Irradiation. Hrs. Mins.	Quanta Absorbed. $\times 10^{-18}$.	Atoms of I. $\times 10^{-18}$.	Quantum Yield.	Temp. °C.
iso-amyl .	0.5150	12 55	6.40	3.76	0.59	16.0
" .	0.6300	13 0	6.50	4.20	0.65	16.5
				Mean =	0.62	
cetyl .	0.3820	14 15	7.10	5.55	0.78	19.0
" .	0.3820	13 0	6.45	4.96	0.77	19.0
" .	0.2080	14 9	7.06	5.00	0.71	19.0
				Mean =	0.75	
methylene	0.5450	12 51	6.40	3.40	0.53	15.5
" .	0.5450	13 27	6.67	3.68	0.55	16.0
" .	0.4100	13 42	6.86	3.94	0.58	16.0
				Mean =	0.55	
tertiary .	0.2200	3 21	10.00	9.52	0.95	15.0
butyl .	0.2310	4 8	12.30	13.00	1.13	15.5
				Mean =	1.04	

taking place more readily than (iii) $\text{R} + \text{I} = \text{RI}$. This might be compared with the Hartel and Polanyi results, because the reaction



like the reaction $\text{Na} + \text{RI} = \text{NaI} + \text{R}$ is dependent on an activation energy which becomes smaller, when among other things, the length of the molecule (carbon chain) increases, or the hydrogen is replaced by halogen, etc. It is easy to speculate on these matters and to draw comparisons, but other possibilities may exist which should not be ignored. It is only assumed (mainly from the absorption spectrum and absence of fluorescence) that a molecule like CH_3I dissociates spontaneously on light absorption. But a polyatomic molecule, as distinct from a diatomic molecule, may have other ways of disposing of its kinetic energy of separation, due to its greater number of degrees of freedom. If the CH_3 radicle is formed it should be capable of reaction. But Bates and Spence found that the addition of hydrogen to the photochemically decomposing CH_3I does not influence the yield, because the collision efficiency of the reaction $\text{CH}_3 + \text{H}_2 = \text{CH}_4 + \text{H}$ compared with $\text{CH}_3 + \text{I} = \text{CH}_3\text{I}$ is relatively very small.¹⁹ This matter surely needs further investigation.

¹⁸ Hartel, Meer and Polanyi, *Z. physik. Chem.*, 1932, 19B, 139.

¹⁹ Hartel and Polanyi, *ibid.*, 1930, 11, 97.

Experiments are now being carried out in this laboratory on the photo-decomposition of mixtures of CH_3I and HI , where the CH_3 radicle, if it is formed, will certainly react with the HI .

Summary.

The quantum yield in the photodecomposition of iodoform in benzene in the absence of oxygen is not greater than unity. The different quantum yields for other iodides have been discussed, and some explanations advanced for the variations.

One of us (K. E. G.) is indebted to the University of Sydney for a Science Research Scholarship enabling him to collaborate in this work.

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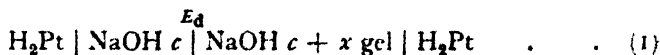
DIFFUSION POTENTIALS AND MOBILITIES OF IONISED GELATIN. PART II. NEUTRAL AND ALKALINE SOLUTIONS.

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In a previous paper,¹ diffusion potentials of gelatin chloride were determined in solutions of about $p_{\text{H}}3$, against solutions of potassium chloride which had been equalised as far as possible, both in salt concentration and in p_{H} . Mobilities of the gelatin kation G' were calculated from these results, which included a few in neutral solutions. The work has now been extended to neutral and alkaline solutions of potassium gelatinate using similar experimental methods.

An important investigation on this subject is that of Ferguson and Schluchter,² who determined the potentials of combinations with and without diffusion:



The difference of (1) and (2) gives the diffusion potentials E_d , which were set up as standing and flowing junctions by manipulating taps in the tubes which connected the two solutions. Sodium hydroxide solutions at concentrations $c = 0.0137, 0.0505$ and 0.0895 N , were treated with gelatin until there was no change in potential, at which point the activity of OH' in the gelatin solution had become constant:

$$\text{i.e.} \quad E = \frac{RT}{F} \log \frac{a_{(\text{OH})_2}}{a_{(\text{OH})_1}} = \text{constant.}$$

A combination with amalgam electrodes:



¹ *Faraday Trans.*, 1935, **31**, I., 349.

² *J. Gen. Physiol.*, 1931-32, **15**, 463.

gave potentials which hardly changed at all with change of x , showing that a_{Na^+} is hardly affected by the substitution of gelatinate by hydroxyl ion. In the present work, this has also been assumed to be true for potassium gelatinate and potassium chloride. When the x/E curves of combinations (1) and (2) become parallel, *i.e.* the diffusion potentials were constant, it was assumed that the alkali was saturated with gelatin. In the 0.0137 *N* solutions this occurred between 20 and 25 g. of gelatin, *i.e.* within the limits 6.85 and 5.48 c.c. of *N*/10 alkali to 1 g. of gelatin. Below these limits alkali is completely combined.

Saturation Capacities for Alkali.

As the amounts of gelatin " x " in Ferguson and Schluchter's experiments were increased, the equivalents of gelatin increased and reached a nearly constant value of 1560 in the 0.0505 and 0.0895 *N* alkali. This holds for solutions containing from 2 to 6 per cent. of gelatin. The 1.0 per cent. solutions have a rather greater saturation capacity, requiring 7.8 c.c. of *N*/10 alkali to 1 g. of gelatin, which corresponds to an equivalent of 1280. By conductimetric titrations, Pauli and Safrin³ find 7.3 c.c. and an equivalent of 1370 for ordinary gelatin, and 5.3 c.c., equivalent 1890 for a sample purified by electroanalysis, which, according to the authors, had had some G^* and G' forms, *i.e.* the most dissociated groups, removed by this treatment. The conductivity method was also used by Stearn,⁴ who finds 7.58 to 7.35 c.c.; equivalent 1320 to 1360.

Mobility of Gelatin in Concentrated Solutions.

In their calculations, Ferguson and Schluchter have treated the gelatin ion as univalent, *i.e.* they consider the motion per equivalent of negatively charged gelatin, and apply the simplified equation:

$$E_d = \frac{RT}{F} \ln \frac{u + v_1}{u + v_2}$$

Values of 0, 20, 40 were assigned to the mobilities of the gelatin anion v_1 (really Fv_1), and it was found that $v_1 = 20$ agreed most closely with the experimental results.

It may be remarked that in these experiments, the maximum amounts of gelatin added gave solutions of gelatin saturated with alkali, containing, *e.g.* 7.7 and 7.4 c.c. of *N*/10 alkali per 1 g. of gelatin, which correspond to solutions at the extreme alkaline end of the neutralisation curve, at which OH' is appreciable, 1×10^{-4} or more, and will therefore have an effect on the transport member. Also all the solutions were so concentrated that activity coefficients were far removed from unity. It seemed of interest therefore to confirm or otherwise the mobilities in dilute solutions, using a different method.

Composition of Solutions.

Solutions were made by adding various quantities of alkali free from carbonate to 1 per cent. gelatinate, and the diffusion potentials were

³ *Biochem. Z.*, 1931, 233, 95.

⁴ *J. Gen. Physiol.*, 1928, 11, 377.

measured against potassium chloride of the same potassium ion concentrations. In neutral solutions, from $p_H = 6$ to $p_H =$ about 8.5, the concentration of the potassium gelatinate was taken as equal to that of the alkali added, $K' = G'$, from 2.8 to $4.4 \times 10^{-3} N$. In such neutral solutions, hydrolysis of potassium gelatinate is low. In the more alkaline solutions, down to $p_H = 10$, (OH') is still of a lower order of concentration, and G' is still nearly equal to K' ($G' = K' - OH'$).

Calculations of Mobilities.

In neutral solutions (I), of KG , concentration c_1 and (II) of KCl concentration c_2 , in which also $c_1 = c_2$, the diffusion potentials are given by :

$$E_{II-I} = \frac{RT}{F} \times (-1) \times \ln \frac{u_{K'} + v_{G'}}{u_{K'} + v_{Cl'}} \quad (1)$$

or
$$E_{II-I} = \frac{RT}{F} \times (-1) \times \ln \frac{x_1}{x_2} \quad (2)$$

in which x_1 and x_2 are the conductivities.

The whole expression is positive, *i.e.* the KCl is positive to the KG , as was found to be the case. In alkaline solutions, the complete Henderson equation may be required (see page 579).

Examples of such calculations are given below. Mobilities (at 25°) selected⁵ are

$$u_{K'} = 73.5, \quad v_{Cl'} = 76.3, \quad u_{H'} = 348, \quad v_{OH'} = 196.$$

By means of equation (1) :

$v_{G'}$	=	0	10	15	20	30	40	50
E_d	=	17.6	14.4	13.0	11.6	9.1	6.8	4.7

The potential, calculated for zero mobility of G' , is identical with the Donnan potential, set up by diffusion of x and K' and Cl' across a surface on one side of which is undiffusible G' . Diffusion will continue until the Donnan equilibrium is established when :

$$x(c_1 + x) = (c_2 - x)^2.$$

Since $c_1 = c_2$ initially, $x = \frac{1}{2}c_2$, and

$$E = 58 \log \frac{c_1 + x}{c_2 - x} = 17.4 \text{ mv.}$$

The same potential should be found also in the more alkaline solutions, when G has zero mobility. For finite mobilities, values differ in neutral and alkaline solutions. Thus, if $p_H = 10$, $(OH') = 1 \times 10^{-4}$ in both solutions, the values of E_d corresponding to a given mobility v , will be greater, *i.e.* at $v = 20$, $E = 13.5$; at $v = 30$, $E = 11.0$; at $v = 40$, $E = 9.10$ mv.

Valency of the Gelatin.

If the gelatin behaves as a multivalent electrolyte, the complete Henderson equation should be used, although the previous workers referred to have not considered this to be necessary. A few calculations on this basis will be added, in order to show how the calculated mobilities will be affected.

⁵ MacInnes, Shedlovsky and Longworth, *J. Amer. Chem. Soc.*, 1932, 54, 2761; Jeffery and Vogel, *Nature*, 1932, 435, 775.

A summary of the equivalent weights of gelatin has already been given. The molecular weight, as estimated by osmotic and other methods, appears to be about 10,300. If it is assumed that this molecule remains undivided on combination, then the total concentrations of the various forms—uncharged, *Zwitterions* and ions—in 1 per cent. solutions is 9.72×10^{-4} . The negative valency of this molecule will increase from 0 to 8.25 as combination with alkali proceeds to saturation. When 1×10^{-4} equivalents of alkali have been added to 1.03 g. of gelatin, the latter has a negative valency of 1. Therefore valency $z = (\text{c.c. of } N/10 \text{ alkali to 1 g. of gelatin}) \times 1.03$.

In the case of the "c" normal solutions of KG and KCl, the Henderson equation applied to multivalent electrolytes takes the form:

$$E_{H-1} = \frac{RT}{F} \frac{(\Sigma u_1 - \Sigma v_1) - (\Sigma u_2 - \Sigma v_2)}{(\Sigma u_1 z_1 + \Sigma v_1 z_1) - (\Sigma u_2 z_2 + \Sigma v_2 z_2)} \ln \frac{(u_1 z_1 + v_1 z_1)}{(u_2 z_2 + v_2 z_2)} \quad (4)$$

In the present case, the only valency differing from unity is that of the gelatin anion z_1 .

In the calculations of the u , v factors, mobilities may be all at 25° or all at 18° C., since ratios of mobilities are only slightly affected by temperature; but finally, of course, E in mv , is calculated at 18° or 25° by the appropriate constant 57.7 or 59.1 respectively. Since each valency, in solutions which have a constant concentration of 1 per cent. gelatin, corresponds to a single concentration of K' and G' , a number of graphs were constructed from equation (4) and integral values of " z ."

POTENTIALS CALCULATED BY EQUATION (4).

z	2	$c = 1.04$	$p_H = 5.7$
v	10	20	30
E_{H-1}	13.7	10.6	8.05
z	3	$c = 2.01$	$p_H = 7.5$
v	10	20	30
E	13.1	9.85	7.3
z	4	$c = 3.88$	$p_H = 9.3$
v	10	20	30
E	12.6	7.15	6.1

Thus the potentials are lower than those calculated by equation (1) for the same mobilities; they fall, although only slightly, as the valency increases on addition of more alkali, and also with increase in v' , the mobility of gelatinate ion. Intermediate valencies lie on interpolated lines, from which v' corresponding to any experimental E may be found.

Example.—At a concentration of 2.6×10^{-3} :

$$z = \frac{2.6 - 1.04}{2.91 - 1.04} \div 2 = 2.68.$$

If $E_d = 10$ mv., v is 20.5 as compared with 27 by equation (1).

Also if $z = 4$, and $E_d = 12.6$, $v = 10$ by the valency formula as compared with 12 by equation (1). Thus mobilities given by the valency formula of the multivalent ions will be about 20 per cent. lower than those per equivalent of gelatin.

In alkaline solutions, the valency equations indicate only slight changes of E with v , thus at $p_H = 10$: $v = 0$, $E = 17.1$; $v = 40$, $E = 15.0$ mv. Since in the alkaline solutions, values of E above 11.0 were not found, it appears that the results of the simple formula are more in accordance with facts presented here.

Experimental.

The purification of gelatin, starting from "coignet gold label" or "best leaf bronze," followed in general the lines indicated in the last paper. For reasons already given, normal *ku* calomel half-cells were used, both in measurements of diffusion potentials, and in those of hydrogen potentials. A Cambridge potentiometer was employed throughout. The indicator of null potential was a Cambridge A.M. galvanometer, short period type, having a sensitivity of 0.35 microvolt per 1 mm. scale deflection at 1 metre.

A stock solution of purified gelatin (5 per cent. or more of gelatin) had previously been analysed by evaporation in platinum, the ash also having been determined. A portion of the melted stock was weighed, and made up with conductivity water to about 50 g. short of the final weight required. Decinormal potassium hydroxide free from carbonate was then added in an amount calculated to give p_H within the neutrality range, which was estimated by a Lovibond comparator (B.D.H. pattern) and standard coloured glasses. If p_H was too low, more measured alkali was added. The

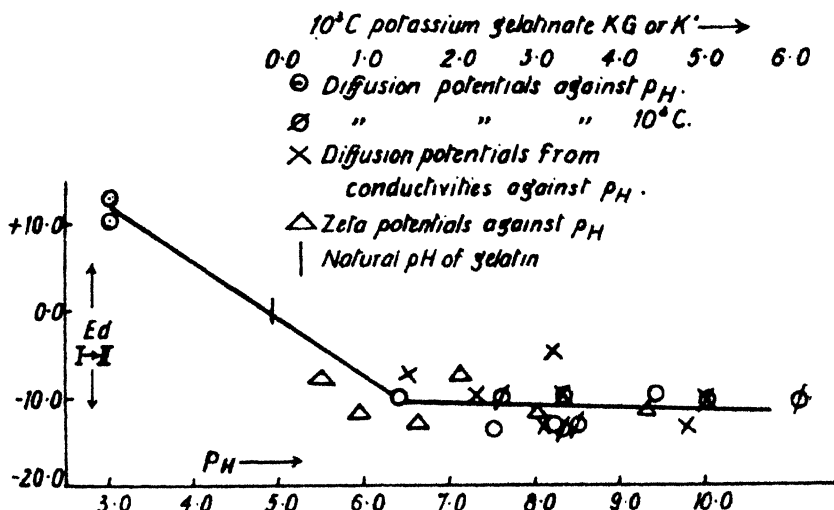


FIG. 1.

solution was then made up to the correct weight with pure water, and the p_H redetermined colorimetrically. A current of hydrogen was started through a sample in a hydrogen electrode vessel of the Sand-Hildebrand type, the potentials being measured at intervals until they became constant, which might require several hours. In the meantime, solution II. of KCl having exactly the same concentration as the KG is made, and if the gelatin solution were definitely alkaline, the required slight excess of alkali was added to the KCl. This solution is not buffered, but retains its alkalinity long enough for a measurement of OH' by the hydrogen electrode. Conductivities (at 28°) of the KCl and KG were then determined in a U tube of high resistance capacity, using the method of Christensen as described by Gram & Cullen.⁶ These conductivities served several purposes *i.e.* :

- (1) A control of the concentration of the KCl.
- (2) A control of the KG, from which also the mobilities of the gelatin ion can be calculated.⁷ These mobilities are subject to rather high errors, being the differences of two larger magnitudes.

⁶ J. Biol. Chem., 1923, **57**, 477.

⁷ Cf. König and Pauli, *Biochem. Z.*, 1932, **252**, 325.

(3) Diffusion potentials could be calculated independently by equation (2) above. The two sets of values, denoted on Fig. 1, by X were sometimes, but not always, in agreement.

Salt bridges were also made containing the KG in jelly form, and the KCl in agar jelly. These were used to avoid all possibility of diffusion of KCl from the normal calomel KCl electrodes to the junction. Finally, the diffusion potentials were measured, with necessary checks. Each experiment with preparations and checks occupied one to two days. A number of such experiments have given additional information as to the relative value of the different junctions.

Static and Flowing Junctions.

In the course of this work, it appeared that the flowing junctions were not so well suited for solutions containing protein ions.

The apparatus with large tap of Ferguson v. Lente and Hitchens,⁸ which had been proved to give excellent results with electrolytes, gave less constant and often very low potentials with gelatin solutions. The relatively large flowing junctions of the MacInnes, Yeh,⁹ and Scatchard type¹⁰ gave rather better results. A large static junction was preferable to either flowing type. In the later experiments these junctions were always used, and were made in a boiling tube having an internal diameter of about an inch. Such junctions are not much affected by complete or partial gelatinisation. Potentials between KG (gel) and KCl were usually, but not always, 1 to 2 millivolts higher than those between KG (sol) and KCl.

Example.—An alkaline solution of KG was made having $[K'] = 0.00606$ $[OH'] = 0.0001$, $[G'] = 0.00596$. The corresponding KCl having

$$[K'] = 0.00608 = [Cl']$$

was buffered with $Mg(OH)_2$, so that $OH' = 0.0004 = \frac{1}{2}Mg''$. Taking into account the $\nu_{Mg} \cdot c_{Mg}$ factor which was only about 1/20 of $\nu_K \cdot c_K$ the full Henderson equation gave:

$$\begin{array}{cccc} E' & 0 & 20 & 30 & 40 \\ E & 17.2 & 13.6 & 11.1 & 8.8 \text{ mv.} \end{array}$$

The observed potential of 0.0 mv. agrees with a mobility of nearly 40.

These results are in fair agreement with those of Ferguson and Schluchter,⁸ obtained in solutions of much higher gelatin concentration.

Comparison with Mobilities Determined by Other Methods.

The mobilities of various proteins have been investigated by a modified Hittorf method in which the changes of concentration after passage of a measured quantity of electricity are determined by micro-Kjeldahl analysis.¹¹ That of ovalbumin rose from 2.1 to 2.8 μ /sec. as the c.c. of N/10 alkali per g. were increased from 5 to 15—a steep rise to a well-defined maximum. Corresponding values for serum albumin were 1.1 at 5 c.c. to a maximum of 2.9 at 15 c.c. Pseudo-globulin gave a flat graph with a maximum of 1.88 at 5 c.c. and $p_H = 10.53$, and then nearly constant velocities with further additions of alkali.

The method of cataphoresis has also been employed. The velocity of ovalbumin rose steadily to 1.0 at $p_H = 6.0$, while that of gelatin increased only slowly,¹² to about 0.8 at $p_H = 6.0$.

⁸ *J. Amer. Chem. Soc.*, 1932, **54**, 1279.

⁹ *Ibid.*, 1921, **43**, 2563.

¹⁰ *Ibid.*, 1925, **47**, 698. ¹¹ König and Pauli, *Biochem. Z.*, 1932, **252**, 325.

¹² Abramson, *J. Gen. Physiol.*, 1932, **18**, 575.

Prideaux and Howitt¹³ also found a steady increase in the velocity of ovalbumin, to 1.92 μ /sec. at $p_H = 9.38$, and a gradual increase in that of gelatin to 0.8 at $p_H = 9.3$. These values must, of course, be multiplied by 9.65 to convert them with electrolytic mobilities. The present values show a rather more rapid increase in the mobility of gelatin, than that found by kataphoresis. If, however, the mobilities of OH' are not introduced into the calculations, the mobilities v' , like the diffusion potentials, remain constant with increasing combination.

Diffusion and Zeta Potentials.

On account of the unfavourable nature of the calculation from potentials to mobilities, it is better to compare the diffusion potentials with zeta, or phase limit potentials of the double layer between the gelatin solution I. and the electrolyte solution II., which takes part in the kataphoretic movement. By the equation of v. Helmholtz and v. Smoluchowski

$$\zeta = \frac{4\pi\eta V}{XK}$$

in which "V" is the velocity, η the viscosity of solutions, K their dielectric constant and X the potential gradient in volts/cm. Putting in the values in c.g.s. units and taking $\eta = 0.01$, $K = 82$, the factor works out at 12.6. Abramson¹⁴ used 12.9. In the present case, a rounded factor of 13 has been used, which gives potentials plotted in Fig. as Δ . Thus, from the velocities of Prideaux and Howitt.¹³

At $p_H = 5.45$	5.93	6.6	7.15	8.0	9.3
$\zeta = 7.8$	11.9	10.6	9.6	11.7	11.7 mv.

Evidently the zeta potentials are of the same order, and vary in the same way as the diffusion potentials. But the mobilities which give rise to identical potentials are quite different according to whether they are related by the phase boundary equations (ζ and v) or by the ionic equations (E and v').

REVIEWS OF BOOKS.

Atomic Physics. By MAX BORN. Pp. xii and 352. Blackie & Sons, Ltd., London. Price, 17s. 6d.

Professor Born's survey of atomic physics is admirably adapted to the needs of junior honours students, and, indeed, students of higher grade will find it helpful in providing a survey, in very moderate compass, of important modern work and ideas.

The kinetic theory of gases, the nuclear atom, wave-corpuscles, atomic structure and spectral lines, electron-spin and Pauli's principle, quantum statistics and molecular structure—these are the principal topics to which the book is devoted.

Mathematical proofs are collected in some thirty appendices, which occupy nearly one hundred pages in a total of three hundred and fifty. Thus, although, as is to be expected, theoretical discussions bulk largely in the book, the arguments developed in the text are not over-laden with mathematical formulae.

The book may be unreservedly commended.

A. F.

¹³ *Proc. Roy. Soc.*, 1929, 126A, 126.

¹⁴ *J. Amer. Chem. Soc.*, 1928, 50, 390.

The Restless Universe. By MAX BORN. Pp. 278. Blackie & Sons, Ltd., London. Price, 8s. 6d.

Professor Born's name has to be added to the long list of those who have endeavoured, with varying degrees of success, to *unscrew the inscrutable*. As was to be expected, his attempt to draw a world-picture which the layman may understand, is highly original. In a text of less than three hundred pages, he starts with a discussion of kinetic theory couched in terms so simple as to demand a picture of a rapidly-emptying classroom to illustrate the meaning of rarefaction. Yet, unhesitating and unrelenting, he carries us along through a description of electrons and ions, waves and particles, atomic structure and nuclear physics to a triumphant conclusion which demands some account of the latest particles and of Pauli's exclusion principle.

Not the least interesting feature of the book is the series of seven moving pictures printed on the specially broad margins of the pages, so that, by rapidly flicking over the pages with the thumb, one is enabled to visualise something of the motion of the electron in the hydrogen atom, or of the flux of the field near a Hertzian oscillator.

A world without models, indeed! *Plus ça change. . . .*

A. F.

Worlds without End. By H. SPENCER-JONES. Pp. xv and 262. English Universities Press, London. Price, 5s. net.

The Astronomer-Royal's introduction to cosmology is *different*. His story, told in plain and telling phrases, opens with an account of the principal astronomical facts and theories concerning the Earth on which we live. Then he gives a similar discussion of the life-history of our nearest neighbour, the Moon, and, proceeding in his argument outward through the cosmos, he tells us of comets and shooting stars, the Sun, our own stellar world, and the extra-galactic universes. There is little space devoted to speculation on origins and endings— an impressive tale is told in unadorned and sober fashion and the reader is left in no doubt about what, in modern astronomy, is well-established theory, and what is not-so-well-established speculation.

The book is an ordered storehouse of essential and fundamental facts, and provides an admirably proportioned picture of our universe as we view it to-day. It is excellently produced and illustrated, and should find a wide circle of appreciative readers.

A. F.

Handbuch der experimental Physik. Bd. xi-2. By W. MEISSNER. Pp. xii and 544. Akad. Verlags M.B.H., Leipzig, 1935. Price, RM. 42. Bound, RM. 44.

This volume is divided into three main sections. The first part deals with resistance measurements for pure metals, alloys and compounds, with the relation between thermal and electrical conductivity, with the effect produced on resistance by magnetic fields and by deformations; with supra-conductivity, and with electron theories, new and old, of electrical conductivity.

The second section is concerned with galvano- and thermo-magnetic effects (Hall, Ettingshausen, Righi-Leduc and Ettingshausen-Nernst effects and their relations), and the third section deals with thermo-electricity.

The volume is encyclopædic in its range, and very few contributions to the subjects of any value have escaped the notice of the authors. Brief but adequate discussions of theoretical matters of primary importance are provided, but the bias of the treatment is, naturally, towards the experimental side.

It is as much a work of reference as a student's handbook—the bibliography is specially full and complete, the number of references exceeding twelve hundred—and is quite indispensable to any serious worker in these fields. The volume is admirably produced, and is an important addition to a series of international repute.

Léemann. Le Pansoma et la Géometrie de l'Énergie. (Georg & Co., Geneva, 1935. Price 15 Swiss francs.)

"Un pansome est une entité énergétique tridimensionnelle, indestructible et indivisible, à délimitation nette par des surfaces pansomiques, à contenu énergétique absolu et constant, la seule variabilité fondamentale qu'il est capable de manifester étant celle de son volume."

In the light of this definition, "sur laquelle nous basons toute notre théorie," the author discourses vaguely and benevolently on the pansomic structure of the atom, on ether and relativity, on radiation, cosmology, the colloid state, causality, karyokinesis, muscular contractions, psychology. . . .

A distinguished Anglican prelate spent some years of his life as the vicar of a parish in the North of England. When, on the occasion of his promotion, he paid a round of farewell visits to his parishioners, he was greeted by a farmer's wife with "I hear as yo're goin', Vicar. Well, if tha hasn't done much good, tha's not done any harm."

Which saying is a parable.

A. F.

Electron Diffraction. By R. BEECHING. (London: Methuen & Co. Pp. viii and 106. Price 3s.)

In this little book the Author has fully maintained the high standard already set up by this series of monographs. The discussion of Kikuchi lines in the earlier part of the book is rather inconclusive, but this is due to present ignorance as to the true nature of these effects. The writer treads very warily when such regions of the subject come under consideration but this is undoubtedly the best thing to do in a small monograph. The sections on crystal structure, atomic scattering factor, and structure factor, could have been more closely woven together, although all the necessary information is certainly present in the book taken as a whole. It is also felt that some further mention could have been made as to experiments on polish effects on metals. Apart from these mild criticisms the work is very complete and is an excellent, up-to-date account of the subject.

J. A. D.

PROPERTIES OF ELECTROLYTIC SOLUTIONS. XVIII. MOLECULAR POLARISATIONS AND POLAR MOMENTS OF SOME ELECTROLYTES IN BENZENE SOLUTIONS.

By JOHN A. GEDDES¹ AND CHARLES A. KRAUS.

Received 23rd December, 1935.

A study of the conductance of solutions of electrolytes in non-polar media² has shown that while such solutions exhibit properties similar to those of solutions of electrolytes in polar media, only a very small fraction of the electrolyte is actually concerned in the conduction process at a given instant—about one part per million. It may be inferred that the bulk of the electrolyte is present in the form of neutral molecules or aggregates which do not contribute to the conduction process. The results at higher concentrations indicate the formation of highly complex aggregates, both charged and uncharged, the degree of complexity increasing with increasing concentration. Molecular weight determinations with solutions of electrolytes in benzene go to show that in the neighbourhood of 10^{-3} *N*, the molecular weight of many electrolytes approximates their formula weight,³ although, depending upon the character of the electrolyte, the degree of complexity may be greater. We thus have conclusive evidence that, in general, electrolytes dissolved in non-polar solvents exist, for the most part, in the form of neutral aggregates comprising two ions at lower concentrations and becoming more complex as the concentration increases. A study of the conductance or of the mean molecular weight of electrolytes fails to give an insight into the structure or nature of these complexes. If, however, the ions exist as such in their two-ion complexes, a study of the dielectric behaviour of solutions of electrolytes in a non-polar medium should give direct information with respect to the existence of such complexes and the change of the molecular polarisation of such solutions with increasing concentration should supply information with respect to the existence of more complex structures.

The earlier investigation of Hooper and Kraus,⁴ on the dielectric behaviour of solutions of electrolytes in benzene, demonstrates, beyond question, that in these solutions electrolytes possess a high polar moment. Thus, we have direct evidence of the existence of ionic dipoles in such solutions.

¹ This paper is based on a thesis presented by John A. Geddes in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Brown University, June, 1935.

² Fuoss and Kraus, *J. Am. Chem. Soc.*, 1933, **55**, 21, 1019, 3614; Kraus, *Trans. Electroch. Soc.*, 1934, **66**, 179.

³ Batson and Kraus, *J. Am. Chem. Soc.*, 1934, **56**, 2017; D. A. Rothrock, Jr., unpublished observations in the Brown Laboratories.

⁴ Hooper and Kraus, *J. Am. Chem. Soc.*, 1934, **56**, 2265.

Unfortunately, in order to be able to interpret the results of dielectric constant measurements of electrolytes in benzene solution with any degree of assurance, it is necessary to carry the measurements to concentrations at least as low as 10^{-4} *N* and the precision in the case of the Hooper and Kraus measurements was not sufficiently high to fix the limiting form of the polarisation curves with certainty. The present investigation has been directed to improving the precision of the measurements and supplying data with respect to the polarisation curves of electrolytes at low concentrations.

Experimental.

Method.—The method employed in the present investigation was that of Hooper and Kraus with some slight modifications. Their method, in turn, was a modification of the resonance method of Wyman.^a The method consists essentially in introducing into the medium a resonator of fixed inductance and capacity. A variable oscillator adjacent to the resonator is adjusted to resonance with the fixed resonator, resonance being indicated by a maximum of the current in the plate circuit of the variable oscillator. To determine the frequency of the oscillator at resonance, it is tuned to known harmonics of a crystal oscillator with which it is inductively coupled, zero beat being indicated in a telephone. In general, the frequency of the resonator will lie between two adjacent harmonics of the crystal oscillator and in order to determine the frequency of the resonator, a small cylindrical condenser, one cylinder of which is mounted on the carriage of a micrometer screw, is introduced into the circuit of the variable oscillator. The frequency of the variable oscillator is a linear function of the setting of the variable condenser. In practice, the condenser is set to a harmonic on one side of the resonance frequency, then to the resonance point, and finally, to the harmonic on the other side of the resonance point. By a linear interpolation between the two harmonics, the frequency of the resonator is obtained in terms of known harmonics of the crystal. If h_0 is the harmonic number of the resonator in air, and h is the harmonic number of the resonator in the medium, then the dielectric constant of the medium is given by the expression: $D = (h_0/h)^2$. The actual frequency of the crystal does not enter. The details of the apparatus have been described by Hooper and Kraus, and need not be given here. It should be mentioned, however, that for the purpose of making connection between the movable cylinder of the precision condenser and the oscillating system, a fixed wire and mercury trough were employed in place of a flexible wire connection. It was found that a flexible connection produces sufficient change in the inductance of the circuit to lead to appreciable variations in the readings.

The resonator consisted of a pair of coaxial brass cylinders connected by a single loop of $\frac{1}{4}$ -inch brass rod. The resonator was silver-plated before use. Its frequency in air was 119 megacycles, which corresponds to a wave-length of 2.52 metres. In order to establish the absence of anomalous dispersion, one series of measurements was carried out with tributylammonium picrate, using a resonator having a frequency of 50 megacycles. The results are given in Table III.(b), and agree with those obtained at the higher frequency within the limits of experimental error.

In carrying out the measurements, the resonator was suspended in pure benzene contained in a cylindrical glass tube having a diameter approximately twice that of the resonator. After determining the resonance point in benzene, a known weight of a dilute solution of the electrolyte was introduced into the benzene by means of a weight burette. After adding the solute, the solution was vigorously stirred, the resonator being lifted above the surface of the solution during the process. After returning

^a Wyman, *Physic. Rev.*, 1930, **33**, 623.

and lifting the resonator out of the solution several times, the latter was again stirred, and this process was repeated until constant readings were obtained for the frequency of the resonator. It is very important that the solution be homogeneous.

The tube containing the solution and resonator was placed in a double-walled tube, through which liquid was circulated by means of a pump from a thermostat whose temperature was maintained constant at 25.00°. The oil jacket was, in turn, placed in a large Dewar tube. Temperatures were in all cases maintained constant within limits set by the precision of the measurements. The variable oscillator was mounted on a pair of rails, and its position with respect to the resonator could be adjusted readily by means of a rack and pinion. The current in the plate circuit of the variable oscillator was read on a milliammeter. The relative position of oscillator and resonator was so adjusted as to give a suitable value of the current. If the current is too low, the maximum cannot be satisfactorily determined, while if the current is too large, the resonance curve of the current is unsymmetrical.

The apparatus permitted of measuring the dielectric constant of solutions reproducibly within a few units in the fifth place of decimals. The absolute variation is somewhat higher at higher than at lower concentrations, probably owing to the fact that with increasing concentration the conductance of the solutions increases, as a result of which the resonance curve becomes appreciably flatter and it is, accordingly, more difficult to locate the maximum.

Materials.—Thiophene-free benzene was washed with concentrated sulphuric acid, water, dilute sodium hydroxide solution and again water. After drying over calcium chloride, it was fractionally crystallised and then refluxed over sodium-lead alloy (10 per cent. Na) in a still from which it was distilled as needed. M.P. 5.48°.

All salts were prepared in the laboratory and purified by recrystallisation from suitable solvents to constant melting-points. The melting-points were as follows: tetraisoamylammonium picrate, 85°; tetraisoamylammonium thiocyanate, 88°; tri-isoamylammonium picrate, 127°; tetra-*n*-butylammonium picrate, 89.5°; tri-*n*-butylammonium picrate, 106°; tetra-*n*-butylammonium perchlorate, 207°; tri-*n*-butylammonium iodide, 102°; tri-*n*-butylammonium bromide, 75°; tri-*n*-butylammonium chloride decomposes without melting at 182°; tetra-*n*-butylammonium acetate, 116°; tetra-*n*-butylammonium bromide, 115.5°; tetra-*n*-butylammonium hydroxytriphenylboron, 145.5°.

Constants.—The density effects due to these organic electrolytes in benzene are small and, rather than to attempt direct measurement of the densities of the extremely dilute solutions, it seemed preferable to measure the densities at higher concentrations and to compute the density values at lower concentrations according to a linear function. The density values as experimentally determined are given in Table I.

TABLE I.—DENSITIES OF SOLUTIONS IN BENZENE AT 25°.

Solute.	N.	d.
Tetraisoamylammonium picrate	0.019	0.8755
thiocyanate	0.042	0.8765
Tri-isoamylammonium picrate	0.027	0.8764
Tetra- <i>n</i> -butylammonium perchlorate	0.010	0.8737
Tetra- <i>n</i> -butylammonium picrate	0.048	0.8771
bromide	0.021	0.8751
acetate	0.003	0.8738
Tri- <i>n</i> -butylammonium picrate	0.099	0.8849
iodide	0.081	0.8815
bromide	0.074	0.8774
chloride	0.095	0.8758
Pure benzene	—	0.8737

TABLE III.—DIELECTRIC CONSTANTS OF SOLUTIONS OF ELECTROLYTES IN BENZENE AT 25.00°.

$f_s \times 10^4$.	D.	P_s .	$f_s \times 10^4$.	D.	P_s .
TRI-ISOAMYLAMMONIUM PICRATE.			TETRA-ISOAMYLAMMONIUM THIOCYANATE.		
0.339	2.26888	3940	0.359	2.26915	4800
0.477	2.26918	3750	0.882	2.27062	4460
0.939	2.27034	3780	1.517	2.27213	4100
1.082	2.27063	3700	2.342	2.27361	3620
1.669	2.27192	3570	3.544	2.27527	3110
1.922	2.27249	3550	5.907	2.27759	2480
2.812	2.27433	3430	9.346	2.27983	1950
2.874	2.27448	3430	TETRA-n-BUTYLAMMONIUM BROMIDE.		
3.995	2.27675	3340	0.503	2.26885	2570
4.818	2.27826	3250	1.030	2.26957	2320
5.953	2.28012	3110	1.180	2.26972	2220
TRI-ISOAMYLAMMONIUM PICRATE.			1.678	2.27015	1970
0.772	2.26987	3680	2.209	2.27063	1840
2.081	2.27286	3560	2.479	2.27077	1730
4.289	2.27731	3310	3.808	2.27174	1530
6.398	2.28116	3140	3.883	2.27177	1510
TETRA-n-BUTYLAMMONIUM ACETATE.			5.522	2.27286	1380
0.741	2.26930	2670	5.563	2.27286	1370
1.231	2.27015	2660	6.739	2.27340	1280
1.706	2.27096	2640	7.146	2.27373	1260
2.182	2.27179	2640	8.547	2.27434	1180
2.565	2.27238	2600	TRI-n-BUTYLAMMONIUM CHLORIDE.		
TRI-n-BUTYLAMMONIUM PICRATE.			2.715	2.26996	1130
0.415	2.26900	3640	3.310	2.27043	1150
0.841	2.26999	3580	5.104	2.27183	1170
1.030	2.27045	3600	5.341	2.27198	1160
1.519	2.27165	3630	7.050	2.27310	1130
1.665	2.27194	3580	8.605	2.27421	1130
2.557	2.27388	3480	8.996	2.27458	1140
2.621	2.27400	3460	12.16	2.27675	1120
3.619	2.27616	3410	15.97	2.27947	1120
3.966	2.27681	3370	TRI-n-BUTYLAMMONIUM BROMIDE.		
4.805	2.27851	3290	1.991	2.26960	1250
4.901	2.27868	3300	3.882	2.27120	1280
6.251	2.28128	3220	4.585	2.27180	1290
6.296	2.28143	3230	6.491	2.27337	1290
TETRA-ISOAMYLAMMONIUM PICRATE.			TRI-n-BUTYLAMMONIUM IODIDE.		
0.191	2.26891	7120	0.885	2.26882	1430
0.465	2.27017	7010	1.796	2.26969	1460
0.734	2.27134	6830	2.798	2.27060	1440
1.223	2.27345	6690	4.201	2.27192	1440
1.818	2.27587	6500	5.666	2.27331	1450
2.239	2.27753	6400	7.085	2.27464	1450
2.876	2.28003	6280	TETRA-n-BUTYLAMMONIUM PERCHLORATE.		
TETRA-n-BUTYLAMMONIUM PICRATE.			0.450	2.26912	3780
0.390	2.26972	6620	0.771	2.26978	3510
0.721	2.27121	6670	0.985	2.27018	3370
1.086	2.27277	6580	1.007	2.27018	3310
1.528	2.27451	6390	1.70	2.27111	2800
2.092	2.27690	6380	1.76	2.27117	2760
2.646	2.27907	6270	1.89	2.27129	2670
3.353	2.28179	6160	2.93	2.27230	2270
TETRA-n-BUTYLAMMONIUM HYDROXY-TRIPHENYLBORON.			3.05	2.27241	2240
0.147	2.26882	8350	3.09	2.27244	2230
0.278	2.26945	7810	4.48	2.27360	1950
0.396	2.27005	7780	4.79	2.27375	1880
0.500	2.27054	7620	4.81	2.27379	1890
0.661	2.27120	7270	6.97	2.27518	1630
			7.50	2.27575	1630

Indices of refraction are not available for determining the correction due to distortion polarisation in the case of the electrolytes employed. Accordingly, values were computed from atomic constants as given in Landoldt and Börnstein's Tables. The error involved, due to uncertainties in these values, is negligible, since the total polarisation is very large in comparison with the correction, which seldom exceeds 1 per cent. The values employed are given in Table II.

TABLE II.—OPTICAL CONSTANTS.

Group	C	H	=O	—O—H	—O—	N≡
Constant (c.c.)	2.418	1.100	2.211	1.525	1.643	2.840
Group	Cl	Br	I	—NO ₂	S	B
Constant (c.c.)	5.967	8.865	13.90	7.30	9.72	3.24

Results.

The experimental results are given in Table III. in which the mol fraction is given in the first column, the observed dielectric constant in the second column, and the molecular polarisation of the electrolyte, calculated as usual according to the Debye formula, in the last column. In making the computations, the dielectric constant of pure benzene is taken to be 2.26800, which corresponds to a polarisation of 26.5392 c.c. All measurements were carried out at 25.00°.

Discussion.

Values of the molecular polarisation for the different salts measured above are shown graphically in Figs. 1, 2, and 3, the polarisation being plotted as ordinate against mol fraction as abscissa. The limiting polarisations for these electrolytes were obtained by extrapolating the curves to zero concentration and values so obtained are given in the second column of Table IV. Polar moments as computed from the polarisation values, corrected for distortion polarisation, are given in column 3, and the distance between centres of charge $\alpha = \mu/4.77 \times 10^{-10}$ are given in the last column.

TABLE IV.—CONSTANTS OF ELECTROLYTES IN BENZENE.

Electrolyte.	P_0 .	$\mu \times 10^{18}$.	$\alpha \times 10^8$.
Tetra- <i>n</i> -butylammonium hydroxytri-phenylboron	8270	19.7	4.13
Tetra-isoamylammonium picrate	7090	18.3	3.82
Tetra- <i>n</i> -butylammonium picrate	6740	17.8	3.73
Tetra-isoamylammonium thiocyanate	5050	15.4	3.23
Tetra- <i>n</i> -butylammonium perchlorate	4250	14.1	2.96
Tri-isoamylammonium picrate	3830	13.3	2.79
Tri- <i>n</i> -butylammonium picrate	3670	13.1	2.74
Tetra- <i>n</i> -butylammonium bromide	2900	11.6	2.43
Tetra- <i>n</i> -butylammonium acetate	2690	11.2	2.35
Tri- <i>n</i> -butylammonium iodide	1440	8.04	1.69
Tri- <i>n</i> -butylammonium bromide	1280	7.61	1.59
Tri- <i>n</i> -butylammonium chloride	1140	7.17	1.50

The first conclusion to be drawn from these results is that, in a non-polar medium, and at relatively low concentrations, electrolytes exist largely as ionic dipoles. The value obtained for the distance between charges is of an order of magnitude such as to indicate that the charges are widely separated, and that the degree of separation depends upon

the size and configuration of the ions. The largest polar moment is obtained for tetra-*n*-butylammonium hydroxytriphenylboron, which is composed of two very large ions. In the negative of this electrolyte, the hydroxyl ion is co-ordinated with the boron atom of triphenylboron. The quaternary ammonium picrates show high polar moments, indicating that, while the charge on the negative ion is doubtless largely localised on the phenolic oxygen atom, it is prevented from approaching closely to the positive charge on the nitrogen atom by the alkyl group surrounding that atom as well as by the nitro-groups adjacent to the phenolic oxygen of the picrate ion. If one of the alkyl groups of the ammonium ions is replaced by hydrogen, as in the case of tri-*iso*amylammonium picrate, for example, the moment is greatly reduced, doubtless because of the closer approach of the phenolic oxygen to nitrogen. Thus, the moment of tetra-*iso*amylammonium picrate is 18.3 Debye units, while that of tri-*iso*amylammonium picrate is only 13.3 D. The distance between charges for the same electrolytes is 3.82 Å and 2.79 Å, respectively, a difference of approximately 1 Å. With the same quaternary ammonium ion, but replacing the picrate ion by the bromide ion, the polar moment is greatly reduced, doubtless due to the smaller size of the bromide ion. Thus, for tetra-*n*-butylammonium picrate, the polar moment is 17.8 D, and for the corresponding bromide, 11.6 D. For tetra-*n*-butylammonium acetate, the polar moment is 11.2 D, only slightly lower than that of the bromide, indicating that the charge is largely localised on the carboxyl group of the acetate ion. Replacing one of the butyl groups of the quaternary bromide by hydrogen leads to a large reduction in the polar moment—from 11.6 D for tetrabutylammonium bromide to 7.61 D for tri-*n*-butylammonium bromide. The polar moments of tri-*n*-butylammonium halides diminish in the order: iodide, bromide, chloride, as is shown by the values: 8.09 D, 7.61 D, 7.17 D; the corresponding distances between charges are: 1.69 Å, 1.590 Å, 1.50 Å. It is clear that as the ions are smaller, the polar moments are likewise smaller. The deformation of the ions must, however, be considerable since, in passing from iodide to bromide to chloride, the change in the distance between charges at each step amounts to only about 0.1 Å. That the deformation should be large is not surprising when we consider the value of the forces concerned. In the case of tri-*n*-butylammonium chloride, the force acting between a pair of charges is of the order of 10^{-8} dyne. If this force were interpreted in terms of pressures, it would be of the order of 10^6 atmospheres. In the case of electrolytes with more complex ions, we probably have not only deformation of electron shells, but also distortion of valence bonds.

According to the form of their polarisation-concentration curves, the electrolytes fall into three groups. In the first group, illustrated in Fig. 1, the polarisation falls off linearly with concentration; in the second group, illustrated in Fig. 2, the polarisation curve falls off rapidly and non-linearly at higher concentration; and in the third group, illustrated in Fig. 3, the polarisation is practically independent of concentration.

To return to the group of electrolytes illustrated in Fig. 1, it will be noted that the curves are, in general, the steeper the greater the value of the polar moment. Fuoss⁶ has derived an equation for the slope dP/df of the polarisation curve for the case of ellipsoidal dipoles. Aside from the constants of the solvent medium, such as dielectric constant,

⁶ Fuoss, *J. Am. Chem. Soc.*, 1934, 56, 1031.

density, and molecular weight, the slope of the curve depends on the moment of the dipole and the two diameters of the ellipsoid. The relation obtained is applicable only so long as λ , the ratio of major to minor diameters, is less than $2^{-1/2}$.

Provided that it is legitimate to consider that, in the case of electrolytes whose plots appear in Fig. 1, the electrical and spatial configurations

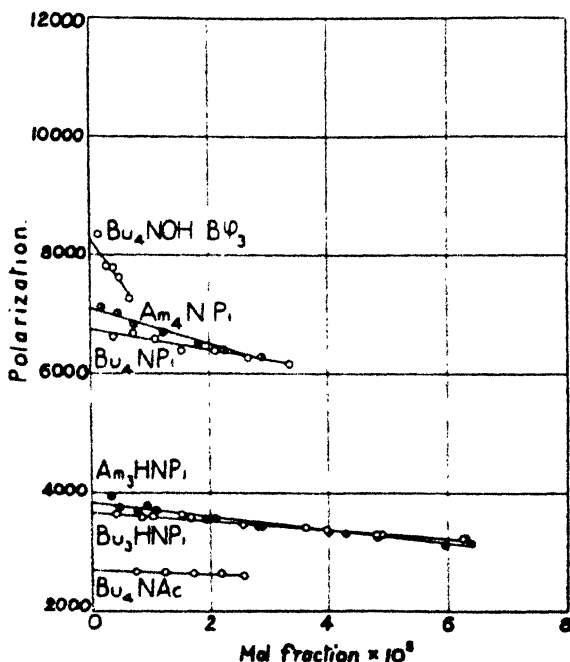


FIG. 1.—Polarisation curves of ionic dipoles which show little tendency to associate.

for the axial ratio, λ , varying between 0.1 and 0.65, the minor diameter varies only between 4.76 Å and 5.17 Å. If we assume an axial ratio of 0.5 (which seems reasonable in view of this computation), we may expect that the values obtained for the minor diameters will be approximately correct. In Table V. are given values of the polar moments, of the slopes dP/df of the polarisation curves and of the diameter of the minor axis λa for the series of electrolytes whose curves appear in Fig. 1.

TABLE V.—COMPUTED MINOR DIAMETERS OF ELLIPSOIDAL MODEL.

Electrolyte.	$\mu \times 10^{18}$.	$dP/df \times 10^{-4}$.	$\lambda a \times 10^8$.
Tetra- <i>n</i> -butylammonium hydroxy-triphenylboron	19.7	-160	6.37
Tetra- <i>iso</i> amylammonium picrate	18.3	-32	6.28
Tetra- <i>n</i> -butylammonium picrate	17.8	-17	6.28
Tri- <i>iso</i> amylammonium picrate	13.3	-12.5	5.05
Tri- <i>n</i> -butylammonium picrate	13.1	-8	5.02
Tetra- <i>n</i> -butylammonium acetate	11.2	-3	4.59

The values obtained for λa , the minor diameter, are reasonable as to order of magnitude. The more complex electrolytes have the larger diameters, and the diameter is relatively independent of the polar moments themselves.

Values of λa may be computed in similar manner from cryoscopic data.⁷ For tri-*iso*amylammonium picrate, the value computed from

freezing-point data is 5.66 Å. in contrast to 5.05 Å as found in the present investigation.

In the case of electrolytes with two relatively symmetrical ions, such as those of the electrolyte appearing in Fig. 2, the polarisation curve falls off very rapidly with concentration. It may be in-

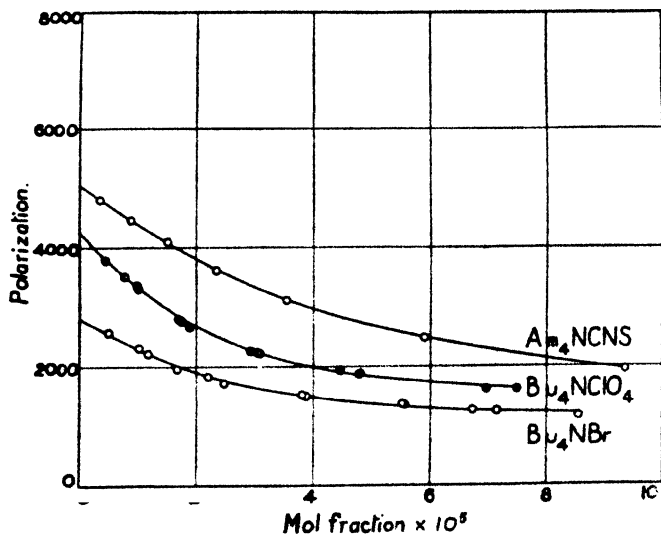


FIG. 2.—Polarisation curves of ionic dipoles which show marked association.

ferred that this is due to the association of dipoles to quadrupoles and more complex structures. Hooper and Kraus⁴ have observed the same type of curve in the case of tetra-*iso*amylammonium bromide and silver

Cryoscopic measurements with salts of this type in dioxane and benzene indicate a high degree of association of these electrolytes at higher concentrations. The molecular weights of tetra-*iso*amylammonium nitrate in dioxane and of the thiocyanate of the

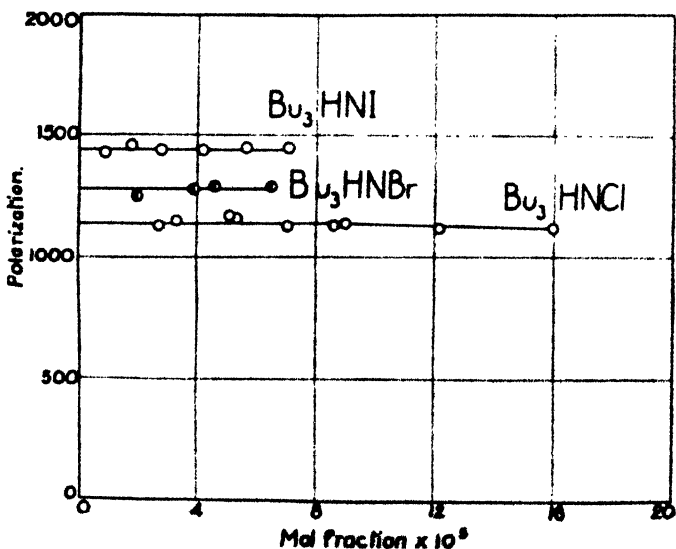


FIG. 3.—Polarisation curves of ionic dipoles which exhibit a complex type of association.

same ion in benzene are several times the formula weight even at concentrations as low as 10^{-3} N. The same is true of tetra-*n*-butylammonium

⁷ Fuoss and Kraus, *J. Am. Chem. Soc.*, 1935, 57, 1.

perchlorate in benzene. At concentrations in the neighbourhood of 10^{-3} *N*, the molecular weight of salts of the type here discussed rises as high as from five to ten times the formula weight, indicating the rapidly increasing complexity of the solute molecules with increasing concentration.

The curves for tri-*n*-butylammonium-iodide, bromide and chloride, as shown in Fig. 3, are practically horizontal, straight lines. One might conclude, on the basis of polarisation data alone, that these dipoles undergo no association. Cryoscopic measurements, however, show clearly that these salts are associated at higher concentrations, although not to as great an extent as the salts illustrated in Fig. 2. Thus, cryoscopic measurements with tri-*n*-butylammonium iodide⁶ indicate an association of 10 per cent. at 10^{-3} *N*, although the polarisation curve indicates no deviations greater than 1 per cent. up to that concentration. At higher concentrations, cryoscopic measurements indicate rapid increase in the complexity of tri-*n*-butylammonium iodide.

Fuoss⁶ has shown that when $\lambda = 2^{-1/3}$ in the ellipsoidal model, the theoretical slope of the polarisation curve is zero. Debye⁹ has shown that for spherical molecules containing a point dipole at the centre, the polarisation increases with concentration, owing to the fact that the dipoles associate end to end. In the case of electrolytes, such as the tri-butylammonium halides, a proper form of the model is probably an approximate sphere with a dipole displaced far to one side of the centre. This case has not been treated theoretically. On the basis of dielectric constant and cryoscopic measurements, we must conclude that association in the case of the tertiary ammonium halides is complex, some of the dipoles associating to form molecules with increased moments, and others associating to form molecules with decreased moments. It is not possible to analyse this case further on the basis of present data.

Summary.

The dielectric constant of solutions of a number of salts in benzene has been measured at low concentrations and polarisation values, as well as polar moments have been computed therefrom.

High values obtained for polar moments, ranging from 7 D. to 20 D., indicate the existence of electrical dipoles in these solutions. According to the form of their polarisation curves, the electrolytes fall into three groups, namely: (1) in which polarisation diminishes linearly with concentration; (2) in which a large and non-linear decrease occurs; and (3) in which the polarisation is independent of concentration. The form of the polarisation curves is related to the structure of the ions of the dipoles concerned, and is determined by association of dipoles to more complex structures. The results of the present measurements are in accord with freezing-point and conductance measurements in the same solvent.

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⁶ D. A. Rothrock, Jr., unpublished observations in the Brown Laboratories

⁹ Debye, *Handbuch der Radiologic* (Marx), Leipzig, 1925, p. 636 ff.

PROPERTIES OF ELECTROLYTIC SOLUTIONS, XIX. CONDUCTANCE OF MIXED ELECTRO- LYTES IN ETHYLENE CHLORIDE. TETRA- BUTYL- AND TETRAMETHYL-AMMONIUM PICRATES.

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I. Introduction.

In solvents of high dielectric constant where association of 1-1 electrolytes is usually negligible, conductances of mixed electrolytes are not additive; it has been shown that the relaxation effect depends on the mobilities and mol-ratios of all species of ions present.² Furthermore, if association occurs, as is the case in most non-aqueous solvents,³ the departure from additivity is still greater if the dissociation constants of the components of the mixture differ appreciably; the dissociation of a weak electrolyte is, to use the phraseology of the Arrhenius theory, repressed by the presence of a strong electrolyte with a common ion.⁴ Both of these effects decrease, of course, with decreasing concentration. It is the purpose of this paper to present data on the conductance of tetramethyl- and tetrabutyl-ammonium picrates, singly and in various mixtures, in ethylene chloride ($D = 10.23$), and to compare the experimental results with theoretical equations which are developed in this paper. This comparison will permit a rigorous cross-check of both theory and experiment. Improvements in experimental technique, which have greatly increased the relative precision and improved somewhat the absolute accuracy of conductance determinations in ethylene chloride, are also described: relative values are now self-consistent within a few hundredths of a per cent., and absolute values are reproducible to about 0.1 per cent.

¹ This paper comprises part of a thesis submitted by Darwin J. Mead in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Brown University.

² Onsager and Fuoss, *J. Physic. Chem.*, 1932, **36**, 2689.

³ Fuoss, *Chem. Rev.*, 1935, **17**, 27.

⁴ The modern theory of association and the older dissociation theory of Arrhenius lead to results that are formally similar in their application, although they differ widely in the underlying mechanisms postulated. The former assumes *a priori* that only ions are present and that these may associate under the action of Coulomb forces provided that the energy relationships permit, the original ions retaining their identity in the associated complex. The dissociation theory of Arrhenius treats the equilibrium of electrolytes from the thermodynamic point of view, assuming that ions are formed from neutral molecules by a process of dissociation. Strictly speaking, no assumptions are here made as to the nature of the neutral molecule, nor of the mechanism involved in the process of dissociation or association. Actually, the older theory assumed the neutral molecules to be combinations of atoms which dissociated with separation of charge to form ions. To be consistent, we should speak of association rather than dissociation constants; we shall, however, retain the conventional nomenclature, since this has been generally employed throughout the literature.

II. Experimental.

Apparatus.—The electrical equipment is essentially the same as that used by Cox, Kraus and Fuoss.⁶ We have supplemented the known resistances available by a 0.1-1.0 megohm non-inductive, non-capacitative resistance⁶ box and take this opportunity to thank Professor M. Wien for his kindness in having the box made for us.

The conductance cells were of the Erlenmeyer type described by Kraus and Fuoss.⁷ The electrodes were unplatinised. Cell constants were determined by comparison with a cell whose constant was 0.38743, according to Jones and Bradshaw's data⁸ for 0.1 demal potassium chloride solution at 25°. The two cells used had constants of 0.10683 and 0.21299, respectively (each an average of five separate determinations which agreed within 0.02 per cent.); polarisation⁹ and lead effects¹⁰ were negligible, since the ratio of cell constants showed a variation of less than 0.05 per cent. with resistance (8000-400,000 ohms) and frequency (400-2000 cycles).

Materials.—Ethylene chloride was purified by the method of Cox, Kraus and Fuoss, with one change: after standing for about a week over activated aluminum oxide in the last step of the purification, the ethylene chloride was separated from suspended oxide by filtering through glass cotton (a very fine glass wool, 2-3 microns average diameter, manufactured by the Owens-Illinois Glass Co., Toledo, Ohio) in an all-glass apparatus designed to exclude atmospheric moisture. This procedure gave consistently lower values of solvent conductance than when the solvent was distilled from the aluminum oxide. The solvent conductance varied from 0.6×10^{-11} to 5.0×10^{-11} mho; since the specific conductance for the most dilute solution was about 5×10^{-7} , the solvent correction was entirely negligible. In view of the uncertainty usually involved in solvent corrections, we are convinced that reliable results in non-aqueous solutions can only be obtained if the correction is made unnecessary by reducing it to a value within other experimental errors.

Tetrabutylammonium picrate (m.p. 89.5°) was prepared by the method of Cox, Kraus and Fuoss, except that the final recrystallisation was made from alcohol (2 c.c. per gram, 85 per cent. yield on first crop).

Tetramethylammonium picrate was prepared by neutralising an aqueous solution of tetramethylammonium hydroxide with an alcoholic solution of picric acid, followed by recrystallisation of the product from 70 per cent. alcohol (11 c.c. per gram, 92 per cent. recovery on first crop). The hydroxide was prepared from the bromide by reaction with silver oxide; the bromide used was obtained by recrystallising Eastman tetramethylammonium bromide twice from 95 per cent. alcohol (18 c.c. per gram, 80 per cent. recovery on first crop).

Method.—All of the series were carried out by a dilution method. The procedure given below is for tetrabutylammonium picrate; on account of the lower solubility of the tetramethyl salt, the initial solutions for this compound and for the mixtures were prepared in a 500 c.c. reservoir, from which about 90 c.c. were pumped into the cell by pressure of dry air saturated with ethylene chloride vapour. (The cell was, of course, previously filled with air saturated with solvent vapour.) This variation was necessary in order to avoid weighing less than 50 mg. of salt.

A sample of salt (about 100 mg., weighed to 0.02 mg.) was weighed into the cell and then about 90 c.c. of ethylene chloride were added. After the salt was dissolved, the cell cap was lifted an instant to release any excess pressure, and the solution was weighed. A correction was applied for the

⁶ Cox, Kraus and Fuoss, *Trans. Far. Soc.*, 1935, **31**, 749.

⁷ Wenk and Wien, *Physik. Z.*, 1934, **35**, 145.

⁸ Kraus and Fuoss, *J. Amer. Chem. Soc.*, 1933, **55**, 21.

⁹ Jones and Bradshaw, *ibid.*, **55**, 1780.

¹⁰ Jones and Christian, *ibid.*, 1935, **57**, 272.

¹¹ Jones and Bollinger, *ibid.*, 1931, **53**, 411.

ethylene chloride in the vapour phase (the solvent has a vapour pressure of about 0.10 atmosphere at 25° and a molecular weight of 98). No reduction to vacuum weights was made, because salt and solvent have about the same density and the weight concentration is obtained as the ratio of weights of solute and solution. In order to obtain volume concentrations, the density¹¹ of ethylene chloride, 1.2455, was used at each concentration, since the highest concentration measured was only several thousandths normal, and the concentrations of the solutions used in the comparison with theory were never greater than $2 \times 10^{-4} N$.

After weighing, the cell was placed in an oil bath at $25 \pm 0.002^\circ$, and allowed to come to temperature equilibrium, after which the resistance was measured. In order to obtain the next (more dilute) solution, a portion of the solution was removed by means of a pipette of the design shown in Fig. 1. The pipette had previously been cleaned, weighed and evacuated.

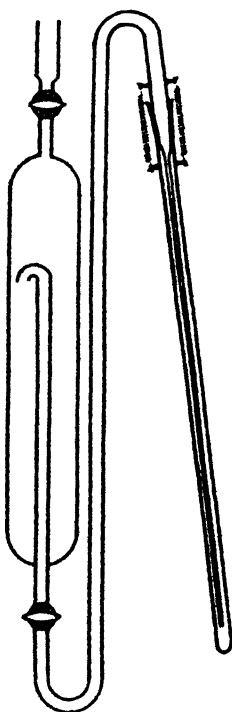


FIG. 1.—Dilution pipette.

The cap was removed and the capillary tip was placed under the surface of the solution in the cell, after which the lower stopcock was opened. After a suitable volume had been drawn into the pipette, the stopcock was closed, the pipette withdrawn from the cell and the cap replaced. Then the stopcock was reopened for a few seconds so that the entering air swept the capillary free of solvent and vapour. The weight then gave the actual weight of solution removed from the cell; a small correction was applied for the difference in density between air (for initial empty pipette weight) and air saturated with solvent (for final weight). The ethylene chloride in the vapour phase in the pipette, of course, counts as solvent removed from the cell. Next, ethylene chloride was added to the cell to bring the volume back to about 90 c.c., and after mixing, the cell was weighed and replaced in the thermostat. The above procedure eliminates errors due to evaporation.

Sorption Effects.—In making a series of dilutions by the method described above, it was found that the conductance values obtained for tetrabutylammonium picrate at concentrations less than $2 \times 10^{-4} N$ were too high when compared with values calculated from points at higher concentrations. This error indicated desorption of electrolyte from the walls and electrodes of the cell, and a careful study of the effect was therefore made, using the method of Cox, Kraus and Fuoss. This consists in making up in a reservoir a series of solutions of the same nominal concentration, and adding successive portions of these to the same cell until the resistance remains the same for repeated fillings of the cell. Points at $1, 2$ and $4 \times 10^{-4} N$ were determined for tetrabutylammonium picrate; the experimental results are summarised in Table I. Since the points at $2 \times 10^{-4} N$ for tetramethylammonium picrate, obtained by the dilution method, were consistent with those at higher concentration, a detailed study of desorption effects was not made for this salt. The results at $2 \times 10^{-4} N$ indicate that $\text{Me}_4\text{N} \cdot \text{Pi}$ is less strongly adsorbed than $\text{Bu}_4\text{N} \cdot \text{Pi}$.

The details of the method are readily made clear by considering the point at $2 \times 10^{-4} N$. Solution A was prepared by adding about 6.5 g. of a 0.0015 N solution of $\text{Bu}_4\text{N} \cdot \text{Pi}$ from a small weight buret to 450 g. ethylene chloride in a Pyrex reservoir. As the results indicate, part of the salt was

¹¹ Walden and Busch, *Z. physikal. Chem.*, 1929, 140A, 89.

TABLE I.—DATA FOR SORPTION EFFECTS IN $\text{Bu}_4\text{N} \cdot \text{Pi}$ SOLUTIONS.

$c = 1.000 \times 10^{-3}$		$c = 2.000 \times 10^{-3}$		$c = 4.000 \times 10^{-3}$	
No.	R.	No.	R.	No.	R.
A 1	398130	A 1	206780	A 1	109580
2	396270	2	206235	2	109270
3	395950	3	206120	3	109290
4	395950	4	206120		
				B 1	109055
B 3	395050	B 1	205640	2	109050
5	395150	2	205680	3	109065
6	395050				
		C 1	205140	C 1	108990
C 1	394260	2	205180		
2	394260	3	205210		
4	394350			Summary.	
		D 1	205210	$c \times 10^3$	Δ (final)
D 2	393950	2	205200	4.000	48.87
3	393970			2.000	51.91
4	393980	E 1	205150	1.000	54.02
E 1	394200				
2	394350				

adsorbed on the walls of the reservoir. When the first portion was added to the cell, further adsorption took place; the resistance dropped with time, and, upon repeated shaking, it became steady at 206780 ohms. Successive fillings with the same solution decreased the resistance by 660 ohms or 0.32 per cent. A second solution was then prepared in the reservoir; the appropriate correction being made for the weighed residue of Solution A remaining in the reservoir. This solution showed a further net decrease of 540 ohms or 0.26 per cent. over the preceding solution. The resistance of Solution C was 470 ohms or 0.23 per cent. less than that of B, while that of Solutions D and E differed from C only within the limit of experimental error. The final value, 205150 ohms, gives 51.91 for the equivalent conductance at $2 \times 10^{-3} N$, which is within 0.03 per cent. of the calculated value. The net change due to adsorption on the glass walls of the cell and reservoir and on the platinum electrodes thus amounted to 0.79 per cent. at $2 \times 10^{-3} N$. The net change at $1 \times 10^{-3} N$ was 0.96 per cent. and at $4 \times 10^{-3} N$ was 0.54 per cent. Desorption produces a smaller absolute error than does adsorption because it represents a differential rather than a total effect; for this reason we were able to obtain fairly reliable data even at 2×10^{-3} by dilution from higher concentrations by the pipette method. (Cf. later comparison of calculated and observed values in the Discussion.)

III. Results.

The experimental results are summarised in Tables II.-IV. Table II.(a) gives the data for tetrabutylammonium picrate; the conductance values are about 2 per cent. higher than those reported by Cox, Kraus and Fuoss, which indicates that the salt used in the previous work may have contained some tertiary salt. (The present material was more carefully purified and melted about 0.5° higher.) Series 1 and 2 were made in different cells by different observers.

The data for tetramethylammonium picrate are given in Table II.(b). The specific conductance κ of the saturated solution at 25° was 2.457×10^{-4} . By making an empirical extrapolation on a $\log \kappa$ - $\log c$ plot (which is nearly linear in this range of concentrations), the saturation concentration was

TABLE II.

Series 1.		Series 2.	
$c \times 10^4$.	Λ .	$c \times 10^4$	Λ .
(a) Conductance of Tetrabutylammonium Picrate in Ethylene Chloride.			
11.708	24.875	15.054	23.140
6.251	29.325	7.187	28.239
3.3525	34.114	3.7710	33.166
1.6131	39.789	1.8761	38.625
0.8732	44.19	0.7810	44.96
0.4268	48.56	0.37668	49.21
0.20877	51.79	0.20363	51.91
0.09995	54.15	0.12281	53.56
(b) Conductance of Tetramethylammonium Picrate in Ethylene Chloride.			
9.977	15.016	8.260	16.019
5.069	19.296	4.509	20.084
3.1691	22.918	2.7627	24.024
1.9900	27.035	1.8822	27.521
1.1186	32.827	1.0879	33.095
0.7677	36.951	0.6230	39.297
0.5124	41.57	0.38626	44.84
0.27331	48.83	0.23732	50.41
0.20321	52.14	0.17528	53.73
19.082	11.713 *	22.25	11.04 **

* Separately determinated.

** Saturated solution.

TABLE III.—CONDUCTANCE OF MIXTURE.

$c \times 10^4$.	$\kappa \times 10^6$.	$c \times 10^4$.	$\kappa \times 10^6$.
(a) $c_{Bu}/c_{Me} = 0.4233$.		(b) $c_{Bu}/c_{Me} = 2.3424$.	
9.178	16.734	9.080	20.826
3.9796	9.461	3.4223	10.187
1.9468	5.760	1.6266	5.792
1.0287	3.6531	1.0670	4.1638
0.6239	2.5257	0.5738	2.5234
0.38856	1.7591	0.41055	1.9102
0.26115	1.2842	0.24736	1.2393
0.18260	0.9583	0.20580	1.0552

TABLE IV.—CONDUCTANCE OF EQUIMOLAR MIXTURE.

$c \times 10^4$.	$\kappa \times 10^6$.	$c \times 10^4$.	$\kappa \times 10^6$.	$c \times 10^4$.	$\kappa \times 10^6$.
$c_{Bu}/c_{Me} = 0.9923$.		$c_{Bu}/c_{Me} = 1.0011$.		$c_{Bu}/c_{Me} = 1.0011$.	
8.797	18.228	8.754	18.209	8.754	18.204
4.1425	10.675	3.9078	10.254	4.674	11.659
2.0418	6.388	2.0238	6.355	2.5557	7.542
1.0348	3.8436	1.1833	4.259	1.5528	5.224
0.6273	2.6118	0.7465	2.9935	0.9425	3.5845
0.4141	1.8779	0.4588	2.0397	0.5810	2.4623
0.26034	1.2838	0.28335	1.3774	0.36121	1.6834
0.20359	1.0438	0.19772	1.0183	0.25100	1.2470
				0.20170	1.0368

found to be 2.22×10^{-2} . Our values for the conductance of this salt average about 0.3 per cent. lower than those of Walden and Busch.¹¹

The data for the mixtures of tetrabutyl- and tetramethyl-ammonium picrate are given in Tables III. and IV.; they include one series at a mol-ratio 0.3/0.7, three at 0.5/0.5 and one at 0.7/0.3. In the first column are given total concentrations, $c = c_{Bu} + c_{Me}$, and in the second the corresponding specific conductances. The heading of each table, c_{Bu}/c_{Me} , gives the molar ratio of tetrabutyl- to tetramethyl-ammonium picrate in the mixture.

IV. Discussion.

It has been shown that the conductance of 1-1 electrolytes as a function of concentration is given at low concentrations by the equation¹²

$$\Lambda = \gamma(\Lambda_0 - \alpha\sqrt{c\gamma}) \quad . \quad . \quad . \quad (1)$$

where γ satisfies the mass action equation

$$c\gamma^2f^2/(1 - \gamma) = K \quad . \quad . \quad . \quad (2)$$

and f is given by the Debye-Hückel limiting equation¹³

$$-\log f = \beta\sqrt{c\gamma} \quad . \quad . \quad . \quad (3)$$

(The limiting equation is used because ions which are not near enough to count as associated ion pairs are, on a time average, far enough apart to permit the above approximation.) The symbols have the following meanings: Λ = equivalent conductance, Λ_0 = limiting conductance, c = concentration, γ = fraction of solute unassociated, f = activity coefficient, α = Onsager's mobility coefficient,¹⁴ β = Debye and Hückel's constant, and K = the "dissociation constant," i.e., the reciprocal of the association constant. By introducing a variable z , defined by the equation

$$z = \alpha\Lambda_0^{-1/2}\sqrt{c\Lambda} \quad . \quad . \quad . \quad (4)$$

(1) may be written

$$\Lambda = \gamma\Lambda_0 F(z) \quad . \quad . \quad . \quad (5)$$

where

$$F(z) = \frac{4}{3} \cos^2 \frac{1}{2} \cos^{-1}(-3\sqrt{3}z/2) \quad . \quad . \quad . \quad (6)$$

(Values for $F(z)$, $0 \leq z \leq 0.209$ have been published in tabular form¹⁵.) Combining (2) and (5), we obtain

$$\frac{F}{\Lambda} = \frac{1}{K\Lambda_0^2} \frac{c\Lambda f^2}{F} + \frac{1}{\Lambda_0} \quad . \quad . \quad . \quad (7)$$

which reduces the conductance curve to a straight line when F/Λ is plotted against $c\Lambda f^2/F$. Equation (7) cannot apply above a critical concentration¹⁶

$$c_\alpha = 3.2 \times 10^{-2} D^3 \text{ at } 25^\circ \quad . \quad . \quad . \quad (8)$$

on account of higher association than pairwise; actually deviations of the order of several tenths of a per cent. appear at somewhat lower concentrations. In ethylene chloride ($D = 10.23$), the critical concentration

¹¹ Fuoss and Kraus, *J. Amer. Chem. Soc.*, 1933, **55**, 476.

¹² Debye and Hückel, *Physik. Z.*, 1923, **24**, 185.

¹³ Onsager, *ibid.*, 1926, **28**, 277.

¹⁴ Fuoss, *J. Amer. Chem. Soc.*, 1935, **57**, 488.

¹⁵ Fuoss, *ibid.*, 1935, **57**, 2604.

is $3.4 \times 10^{-4} N$. In Fig. 2, a plot of our data for the dilute solutions of tetramethyl- and tetrabutyl-ammonium picrates is given; it will be seen that the data give straight lines as required by (7). The slope and intercept of the lines give, respectively, $1/K\Lambda_0^3$ and $1/\Lambda_0$, which, in turn, evaluate K and Λ_0 . (For details of the method of calculation, see p. 36, ref. 3.) The results are given in Table V.

TABLE V.—CONSTANTS FOR $\text{Me}_4\text{N} \cdot \text{Pi}$ AND $\text{Bu}_4\text{N} \cdot \text{Pi}$ IN $\text{C}_2\text{H}_4\text{Cl}_2$.

Salt.	Intercept.	Slope.	$K \times 10^4$.	Λ_0 .
$\text{Me}_4\text{N} \cdot \text{Pi}$	0.013549	5.038	0.3256	73.81
$\text{Bu}_4\text{N} \cdot \text{Pi}$	0.017421	1.3337	2.2756	57.40

A comparison of calculated and observed values is shown in Tables VI and VII. In the first column are given concentrations and in the second per cent. deviations,

$$\Delta = \left(\frac{F}{\Lambda_{\text{calc.}}} - \frac{F}{\Lambda_{\text{obs.}}} \right) \cdot 100 \frac{\Lambda_{\text{calc.}}}{F},$$

when the deviation is positive, Λ (obs.) $>$ Λ (calc.).

The data for $\text{Me}_4\text{N} \cdot \text{Pi}$ are somewhat more self-consistent than those

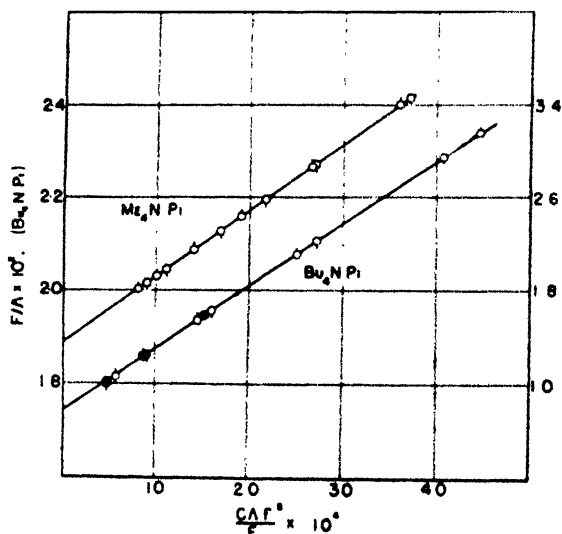


FIG. 2.—Test of conductance equation (7) for tetramethyl- and tetrabutyl-ammonium picrates in ethylene chloride. Black circles are final points from Table I.

for $\text{Bu}_4\text{N} \cdot \text{Pi}$. The large deviations at about $2 \times 10^{-4} N$ indicate that the theoretical equation is beginning to fail; at 3.4×10^{-4} , according to (8), it would be impossible to calculate the conductance by means of (5). Our value for Λ_0 , 73.81, for $\text{Me}_4\text{N} \cdot \text{Pi}$ is 1.5 per cent. lower than the Λ_0 value obtained by Walden and Busch;¹¹ of this discrepancy, 0.3 per cent. is due to a difference in absolute values of specific conductance, and the remaining 1.2

per cent. is due to Walden and Busch's method of extrapolation. When mass action effects are present, an inflection point appears in the $\Lambda \cdot \sqrt{c}$ curve at approximately

$$c_{\text{inf.}} = 0.2165 K/f^3_{\text{inf.}}$$

For $\text{Me}_4\text{N} \cdot \text{Pi}$ in $\text{C}_2\text{H}_4\text{Cl}_2$, $c_{\text{inf.}}$ is about $7.5 \times 10^{-6} N$. Near the inflection region, the curve approximates linearity, and Walden and Busch simply

extrapolated from their most dilute points linearly with a slope equal to 5430, in order to obtain their value of Λ_0 . As a matter of fact, the curve must approach Λ_0 at $c = 0$, with a slope equal to 547, the Onsager coefficient, and be concave to the axis of concentration in the region between $c = 0$ and the inflection point.

In the case of the tetrabutyl salt, the theoretical equation seems to hold to slightly higher concentrations than for the tetramethyl salt. The large deviations at 0.9995 and $1.2281 \times 10^{-4} N$ are due to desorption in diluting the more concentrated solutions. At each of these points, the concentration is calculated by the product of dilution ratios from the initial concentration used in the series; when desorption occurs, the specific conductance (and hence Λ) is too large, because more electrolyte (and hence ions) is actually present than is calculated from dilution ratios. The relative error due to desorption increases with dilution. The last three points of Table VII. are those which were discussed in the section on Sorption Effects. These values are independent determinations, *i.e.*, they do not depend on a product of dilution ratios as do those in the series. It will be noted that they agree well with the calculated values, which are based on the average straight line of Fig. 2 drawn through all of the points.

TABLE VI.

TABLE VII.

COMPARISON OF CALCULATED AND OBSERVED CONDUCTANCES.

$c \times 10^4$	Δ	$c \times 10^4$	Δ
(a) $\text{Me}_4\text{N}^+ \text{Pi}^-$		$\text{Bu}_4\text{N}^+ \text{Pi}^-$	
19.900	-0.16	16.131	-0.03
11.186	0.00	8.732	-0.06
7.677	+0.05	4.268	+0.03
5.124	+0.05	2.0877	+0.04
2.7331	+0.02	0.9995	+0.31
2.0321	0.00	18.761	-0.08
18.822	-0.37	7.810	+0.01
10.879	0.00	3.7668	+0.04
6.230	-0.04	2.0363	+0.10
3.8626	0.00	1.2281	+0.20
2.3732	-0.03	4.000	-0.03
1.7528	0.00	2.0000	-0.03
		1.0000	+0.07

We next consider the mixtures. As was pointed out in the introduction, two effects combine to prevent the specific conductances from being additive: mobility effects due to mixed ionic atmospheres, and the common ion effect which promotes increased association of the relatively small tetramethylammonium ion. Both effects decrease with decreasing concentration, and at zero concentration, both components have the Λ_0 values characteristic of the pure salts. The differential mobility effect is greater the more the mobilities of the ions of like charge differ, and vanishes for the case of equal mobility of ions of like charge. In our example, the common ion effect predominates, because the total ion concentration is so small that the net mobility effect amounts to only about 4 per cent. at the highest concentration considered, and the mixed atmosphere effect is superimposed on this correction. As will be seen below, however, the effect is large enough to be observable at $1 \times 10^{-4} N$

in ethylene chloride. At higher concentrations, the effect would, of course, be larger, but we are unable to make the theoretical calculation because no theory is yet available.

The theory for the first effect has been developed by Onsager and Fuoss; that for the second is easy to derive. Suppose we have two salts AX (methyl) and BX (butyl) with a common negative ion X'. Let c_1 be the stoichiometric concentration of AX and K_1 its dissociation constant, and c_2 and K_2 the corresponding quantities for BX. Then at a total concentration c , we have

$$c = c_1 + c_2 \quad . \quad . \quad . \quad . \quad (9)$$

$$[A^+] = \gamma_1 c_1, [B^+] = \gamma_2 c_2 \quad . \quad . \quad . \quad . \quad (10)$$

$$[A^+] + [B^+] = [X'] = c_1 \gamma_1 + c_2 \gamma_2 \quad . \quad . \quad . \quad . \quad (11)$$

$$[AX] = c_1(1 - \gamma_1), [BX] = c_2(1 - \gamma_2) \quad . \quad . \quad . \quad . \quad (12)$$

where the bracketed quantities mean the actual concentrations of the species enclosed. We then have two mass action equations to satisfy simultaneously

$$\gamma_1(c_1 \gamma_1 + c_2 \gamma_2) f^2 / (1 - \gamma_1) = K_1 \quad . \quad . \quad . \quad . \quad (13)$$

$$\gamma_2(c_2 \gamma_2 + c_1 \gamma_1) f^2 / (1 - \gamma_2) = K_2 \quad . \quad . \quad . \quad . \quad (14)$$

where the activity coefficient is given by the equation

$$-\log f = \beta \sqrt{c_1 \gamma_1 + c_2 \gamma_2} \quad . \quad . \quad . \quad . \quad (15)$$

If r denotes the ratio K_1/K_2 , we have the simple relation between the γ 's:

$$\gamma_1(1 - \gamma_2) / \gamma_2(1 - \gamma_1) = r \quad . \quad . \quad . \quad . \quad (16)$$

If we use (16) to eliminate γ_2 from (13) except in f^2 , we obtain the cubic equation

$$\gamma_1^3 + \left(\frac{r+x}{1-r} + \gamma \right) \gamma_1^2 - \frac{1-2r}{1-r} \gamma \gamma_1 - \frac{r\gamma}{1-r} = 0 \quad . \quad (17)$$

where

$$x = c_2/c_1 \quad . \quad . \quad . \quad . \quad (18)$$

and

$$\gamma = K_1/f^2 c_1 \quad . \quad . \quad . \quad . \quad (19)$$

For simplicity, this may be written

$$\gamma_1^3 + b_1 \gamma_1^2 + b_2 \gamma_1 + b_3 = 0 \quad . \quad . \quad . \quad . \quad (20)$$

Now (17) is not a pure algebraic equation, because γ_1 appears as an exponent in f^2 , nor has γ_2 been eliminated from f^2 . It is possible, however, by a series of successive approximations to solve (17) and (16) for γ_1 and γ_2 , given c_1 , c_2 , K_1 , K_2 , r and x . The details of this calculation will be illustrated by a numerical example.

Suppose we have a mixture of tetramethyl- and tetrabutyl-ammonium picrates for which x , the ratio of butyl to methyl, is 0.4233, and where $c = 1.0287 \times 10^{-4}$. For this pair of salts, $r = 0.3256/2.2756 = 0.14308$. From the values of the constants given in Table V., we find, by means of (1), (2) and (3), that $\gamma = 0.8114$, $f^2 = 0.6360$ for pure $\text{Bu}_4\text{N}^+\text{Pi}^-$ at $c = 1.0287 \times 10^{-4}$ and $\gamma = 0.4813$, $f^2 = 0.7058$ for pure $\text{Me}_4\text{N}^+\text{Pi}^-$ at the same concentration. If we use the average¹⁷ of the f^2 values, 0.6709,

¹⁷ A better approximation could have been obtained by interpolating for f^2 linearly on a mol fraction scale, but the final values of γ_1 and γ_2 are, of course, independent of the initial approximations.

as a first approximation, (17) becomes

$$\gamma_1^3 + 1.3324 \gamma_1^2 - 0.5593 \gamma_1 - 0.11210 = 0,$$

which gives $\gamma_1 = 0.4522$. This gives $\gamma_2 = 0.8523$ by (16), and we now calculate f^2 in second approximation by (15), using these values of γ_1 and γ_2 . This gives $f^2 = 0.6841$ as second approximation, and (17) becomes

$$\gamma_1^3 + 1.3195 \gamma_1^2 - 0.5485 \gamma_1 - 0.10995 = 0.$$

The root is $\gamma_1 = 0.4488$, which gives $\gamma_2 = 0.8505$ and $f^2 = 0.6848$. Returning this value to (17) leads to $\gamma_1 = 0.4485$, $\gamma_2 = 0.8504$, unchanged by further repetition of the process, as the fraction of tetramethyl- and tetrabutyl-ammonium picrates existing as free ions in the mixture.

In order to compute the mobility correction by the method of Onsager and Fuoss¹⁸, we need values for the single conductances. If we assume Walden's rule to hold for the picrate ion, and using Ulich's¹⁹ value $\Lambda_0(\text{Pi}')\eta = 0.268$, $\Lambda_0(\text{Pi}')$ in ethylene chloride is $34.12 = \Lambda^\circ$, using $\eta_{25} = 0.007853$. Then $\Lambda^\circ_1 = 39.69$ for Me_4N^+ and $\Lambda^\circ_2 = 23.28$ for Bu_4N^+ . We then have, in Onsager and Fuoss' notation, for the matrix giving the mobility-ratios

$$\omega_{ji} = \Lambda^\circ_j / (\Lambda^\circ_j + \Lambda^\circ_i),$$

the quantity

$$(\omega_{ji}) = \begin{pmatrix} 0.5000 & 0.6303 & 0.5377 \\ 0.3697 & 0.5000 & 0.4056 \\ 0.4623 & 0.5944 & 0.5000 \end{pmatrix}$$

The μ 's [4.7.2] have the values $\mu_1 = c_1\gamma_1/2(c_1\gamma_1 + c_2\gamma_2) = 0.2774$, $\mu_2 = 0.2226$, $\mu_3 = 0.5000$. For the matrix \mathbf{H} , with elements [4.9.9]

$$h_{ji} = \mu_i \omega_{ji} + \mu_0 \omega_{0j} \delta_{ji},$$

we obtain

$$(h_{ji}) = \begin{pmatrix} 0.5909 & 0.0823 & 0.2312 \\ 0.1749 & 0.6947 & 0.2972 \\ 0.1492 & 0.0903 & 0.7395 \end{pmatrix}$$

with the invariants [4.9.5] $I_1 = 2.0250$ and [4.9.6] $I_2 = 1.2853$. For operation on eigenvectors [4.9.7], [4.9.8] of \mathbf{H} ,

$$1 - H^{1/2} = 0.6432 - 0.6992 H$$

according to the proof in § 4.9 of Onsager and Fuoss' paper. In ethylene chloride, the relative mobility correction [4.7.10] due to relaxation effects is given by

$$-\Delta X_i/X = 11.693 \Gamma^{1/2} Z'_i (1 - H^{1/2})_{i0} r_{0i},$$

where Γ is total ionic concentration, $2(c_1\gamma_1 + c_2\gamma_2)$. We find $\Delta X_1/X = -0.0423$, $\Delta X_2/X = -0.0307$ and $\Delta X_3/X = -0.0371$. In pure

¹⁸ The method of calculation is fairly simple from the point of view of arithmetical manipulation, but the underlying theory is somewhat too complicated to be explained in detail here. For this reason, the reader is referred to the original paper by Onsager and Fuoss for an explanation of the method and symbols; to facilitate reference, equation numbers in square brackets will be given which correspond to those used in the cited paper. The electrophoresis correction is derived in § 4.2; in §§ 4.3-4.7, the differential equations for the relaxation effect are set up and solved; and in §§ 4.8-4.10, the method of calculation is explained. In order to read § 4.3, it is necessary first to read §§ 2.1-2.5, but the material in section 3 (pp. 2704-2735) deals primarily with viscosity effects, and may be omitted by those interested only in the conductance theory.

¹⁹ Ulich, *Trans. Far. Soc.*, 1927, 23, 388.

$\text{Me}_4\text{N} \cdot \text{Pi}$ or pure $\text{Bu}_4\text{N} \cdot \text{Pi}$ at a total ionic concentration of 1.1688×10^{-4} the actual ionic concentration in the mixture under discussion, the relaxation correction for either ion would be 3.71 per cent. In the mixture, the correction for the tetramethyl ion is increased to 4.23 per cent., and that for the butyl decreased to 3.07 per cent.; that is, the faster ion is slowed down and the slower ion is accelerated. Multiplying Λ° , by the appropriate $\Delta X_i/X_i$, we find $\Delta\Lambda_1 = 1.677$, $\Delta\Lambda_2 = 0.715$, $\Delta\Lambda_3 = 1.267$ for the relaxation corrections. We also have to apply a correction

$$[89/\eta(DT)^{1/2}](c_1\gamma_1 + c_2\gamma_2)^{\dagger}$$

to each Λ° , for electrophoresis [4.2.11], which amounts to 0.723 in this case. We thus obtain $\Lambda'_1 = 37.290$, $\Lambda'_2 = 21.841$ and $\Lambda'_3 = 32.130$ as the ionic conductances for (hypothetical) complete dissociation. In order to calculate the specific conductance, we have

$$1000\kappa = c_1\gamma_1\Lambda'_1 + c_2\gamma_2\Lambda'_2 + (c_1\gamma_1 + c_2\gamma_2)\Lambda'_3 = 3.6543 \times 10^{-3} \quad (21)$$

The observed value of specific conductance at this concentration was 3.6531×10^{-3} , which agrees within 0.03 per cent. with the value calculated above.

If the effects of mixed ionic atmospheres are neglected, a somewhat larger value is obtained

$$\begin{aligned} 1000\kappa' &= c_1\gamma_1(\Lambda_1^\circ - 0.0371\Lambda_1^\circ - 0.723) + \\ &\quad c_2\gamma_2(\Lambda_2^\circ - 0.0371\Lambda_2^\circ - 0.723) + \\ &\quad (c_1\gamma_1 + c_2\gamma_2)(\Lambda_3^\circ - 0.0371\Lambda_3^\circ - 0.723) = 3.6578 \times 10^{-3} \end{aligned}$$

which is 0.068 per cent. larger than the correctly computed value. If we calculate the value κ'' obtained by adding the specific conductances of each salt present alone at its actual concentration, we obtain the specific

TABLE VIII.—COMPARISON OF CALCULATED AND OBSERVED SPECIFIC CONDUCTANCES FOR MIXTURES.

$c \times 10^4$	Δ	$c \times 10^4$	Δ
$c_{\text{Bu}}/c_{\text{Me}} = 0.4233$		$c_{\text{Bu}}/c_{\text{Me}} = 1.0011$	
1.0287	— 0.03	Series 1.	
0.6239	+ 0.01		
0.38856	+ 0.03	1.5528	— 0.27
0.26115	+ 0.02	0.9425	— 0.10
0.18260	— 0.02	0.5810	— 0.05
		0.36121	+ 0.02
$c_{\text{Bu}}/c_{\text{Me}} =$	0.9923	0.25100	+ 0.03
		0.20170	— 0.01
1.0348	— 0.21	Series 2	
0.6273	— 0.15		
0.4141	— 0.11		
0.26034	— 0.12	1.1833	— 0.23
0.20359	— 0.12	0.7465	— 0.14
		0.4588	— 0.10
$c_{\text{Bu}}/c_{\text{Me}} =$	2.3424	0.28335	— 0.11
		0.19772	— 0.13
1.0670	— 0.17		
0.5738	— 0.09		
0.41055	— 0.09		
0.24736	— 0.07		
0.20580	— 0.08		

conductance the solution would have if there were no interaction at all. For $x = 0.4233$ and $c = 1.0287 \times 10^{-4}$, $c_1 = 0.7228 \times 10^{-4}$ and $c_2 = 0.3059 \times 10^{-4}$. At 0.7228×10^{-4} N, $\text{Me}_4\text{N} \cdot \text{Pi}$ has a specific conductance of 2.7177×10^{-6} ; and at 0.3059×10^{-4} N, $\text{Bu}_4\text{N} \cdot \text{Pi}$ has a specific conductance of 1.5353×10^{-6} , giving $\kappa'' = 4.2530 \times 10^{-6}$, a value 16.40 per cent. greater than the correct value. Finally, we obtain κ''' , the additive value by linear interpolation on a mol-ratio scale:

$$\kappa''' = \frac{x}{1+x} \kappa_{\text{Bu}} + \frac{1}{1+x} \kappa_{\text{Me}} \quad (22)$$

At 1.0287×10^{-4} , $\kappa(\text{Bu}_4\text{N} \cdot \text{Pi})$ is 4.4347×10^{-6} and $\kappa(\text{Me}_4\text{N} \cdot \text{Pi})$ is 3.4638×10^{-6} , giving $\kappa''' = 3.7526 \times 10^{-6}$ which is 2.62 per cent. too large.

A similar calculation has been made at each of the points in the dilute range for the mixtures given in Tables III. and IV. This calculation is summarised in Table VIII. The percentage deviation Δ is defined as $100 (\kappa_{\text{obs.}} - \kappa_{\text{calc.}}) / \kappa_{\text{calc.}}$. It will be noted that the agreement is within

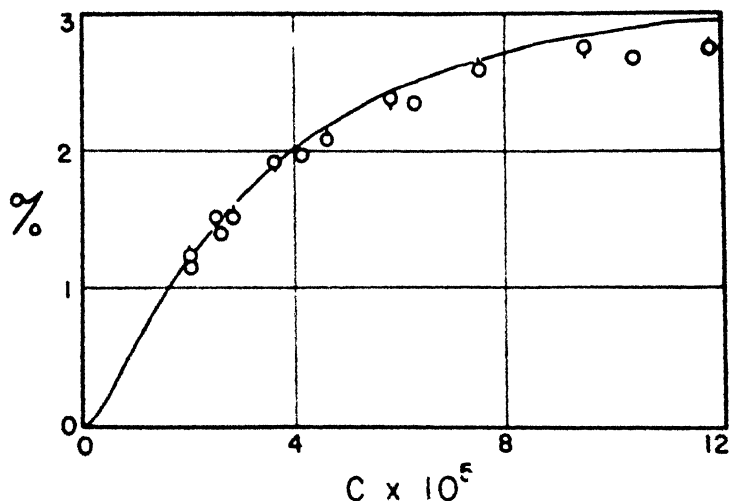


FIG. 3.—Percentage difference between true and linearly additive specific conductances for equimolar mixture of tetrabutyl- and tetramethyl-ammonium picrates in ethylene chloride at 25° as a function of concentration. Solid curve calculated, circles observed (Table VIII.).

the experimental error in every case; the observed values contain the errors in the actual measurements on the mixtures while the calculated values naturally contain, through the two Λ_0 and K values, the sum of the experimental errors involved in the determinations on the pure salts.

The difference between the actual value of specific conductance in a mixture and the value calculated by (22), i.e., by the simplest mixture rule, is a rather interesting function of concentration and mol-ratio. In Fig. 3, the solid curve is the calculated value of $100 (\kappa''' - \kappa) / \kappa$ for an equimolar mixture ($x = 1$), plotted against concentration, and the circles represent the experimentally determined values. At zero concentration, where there is no association,

$$\lim \kappa / c = \lim \kappa''' / c \quad (23)$$

It can easily be shown that

$$\left(\frac{d \text{ } 1000 \kappa}{dc}\right)_{c=0} = \frac{\Lambda_1^\circ + \Lambda_2^\circ}{1+x} + \frac{x(\Lambda_2^\circ + \Lambda_3^\circ)}{1+x} \quad (24)$$

and that

$$\left(\frac{d(\kappa''' - \kappa)/\kappa}{dc}\right)_{c=0} = 0. \quad (25)$$

If specific conductance at a fixed concentration is plotted against mol fraction, a curve is obtained which is convex towards the axis of mol fraction. The line joining the end points represents κ''' . At high concentrations, $\kappa(\text{Bu}) > \kappa(\text{Me})$ on account of the higher dissociation of the butyl salt, while at low concentrations, where dissociation is nearly complete, $\kappa(\text{Bu}) < \kappa(\text{Me})$, because the Me_4N^+ ion has a greater mobility than the Bu_4N^+ ion. The per cent. difference between κ and κ''' has a maximum value which is at about 70 per cent. $\text{Me}_4\text{N}^+\text{Pi}$; 30 per cent. $\text{Bu}_4\text{N}^+\text{Pi}$ at $10^{-4} N$, and which shifts with concentration. It is possible to derive the corresponding equation, but since it is quite complicated, and does not contain much in the way of new information, it will not be discussed here. At the concentration where $\kappa(\text{Bu}) = \kappa(\text{Me})$, the conductance curves for the pure components cross on a $\Lambda - \sqrt{c}$ plot. At this concentration, the equation

$$\frac{\gamma_{\text{Me}} F(z_{\text{Me}})}{\gamma_{\text{Bu}} F(z_{\text{Bu}})} = \frac{\Lambda_0(\text{Bu})}{\Lambda_0(\text{Me})} \quad (26)$$

must be satisfied. (Here $F(z)$ is the function specified in Equation (6).) The curves cross at $c = 2 \cdot 10 \times 10^{-8}$, which gives 0.7783 for the left-hand side of (26). From the values of the limiting conductances obtained by extrapolation on a $F/\Lambda - c\Lambda f^2/F$ plot, we find for the right-hand side $57.40/73.81 = 0.7777$. The agreement is within 0.1 per cent. which is within the error of locating the concentration by graphical interpolation on the $\Lambda - \sqrt{c}$ plots.

Summary.

An improved technique for determining conductance of solutions in volatile solvents is described. Relative values, self-consistent to several hundredths of a per cent were obtained.

The conductance of tetrabutylammonium picrate, of tetramethylammonium picrate and of various mixtures of these salts in ethylene chloride have been determined. Up to about $10^{-4} N$, conductance values for the mixtures, calculated from the constants Λ_0 and K of the pure salts by an extension of the association theory to mixtures, agree with the observed values within the experimental error of about 0.1 per cent.

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ELECTRON DIFFRACTION ANALYSIS OF THE ORIENTATION OF THE MOLECULES OF LUBRICATING OILS.

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The object of lubrication is the reduction of friction and there are two main methods of achieving this end. It has been shown by the experiments of Tower¹ and the theoretical investigation of his results by Osbourne Reynolds² that a well-lubricated journal or shaft becomes automatically separated from its bearing by a film of liquid oil under pressure when it is rotating at normal speeds, and the frictional resistance is then entirely due to the viscosity of the oil. This type of lubrication is known as "liquid film" or "viscous lubrication."

However, in many cases, it is impossible to design the bearings of any machine so that they shall automatically maintain a thick film of oil between the contacting surfaces. Under these circumstances, when the solid surfaces actually rub against one another, the efficiency of an oil as a lubricant is found to depend no longer upon the viscosity but upon a new property of the lubricant often termed its "oiliness." This type of lubrication is known as "solid film" or "boundary" lubrication.

In boundary lubrication, the lubricating film, though excessively thin, may be several molecules thick and it has been shown that oiliness is an expression of the fact that the molecules of an efficient lubricant become oriented on the bearing surfaces, producing films which have a very low coefficient of friction when the bearing surfaces are in contact.

Determinations of the viscosity, specific gravity, volatility, flash point, etc., give valuable information regarding the performance of a lubricant. None of these tests, unfortunately, measure the degree of oiliness upon which the reduction of friction at low speeds and under high pressures depends. This property has, hitherto, been only measured by friction-testing machines.

Since the orientation of the molecules of long-chain carbon compounds can be detected from the electron diffraction patterns obtained by reflecting a beam of electrons from a film of the compound, an attempt was made to arrange a number of oils in an order of *decreasing* degree of orientation by the Electron Diffraction method, and then to compare this order with their efficiencies as boundary lubricants as found in practice.

Method.

Specimens of the various oils were spread out in thin films upon metal backings and inserted in an Electron Diffraction apparatus similar in design to that described by Professor G. P. Thomson.³ A fine beam of electrons was passed from the discharge tube, through two small pin-holes

¹ Tower, *Proc. Inst. Mech. Eng.*, 1883, 632; 1884, 29; 1885, 58; 1888, 173; 1891, 111.

² *Phil. Trans.*, 1886, 157.

³ G. P. Thomson and Fraser, *Proc. Roy. Soc.*, 1930, 128A, 641.

in the anode, and was incident at a small grazing angle on the specimen. The energy of the electrons used was about 30,000 volts.

Preparation of Films.

Thick films of the oils were prepared by allowing a drop of the lubricant to spread over the surface of the backing when the latter was placed on a level surface.

Very thin films were prepared by rubbing the backing, which had been smeared previously with a little of the oil under test, with soft tissue paper until a thin uniform film was obtained. This method was employed by Murison.⁴

Only rough estimates of the thickness of the films used can be given. In the apparatus, the thicker films tended to flow to one end of the specimen. The thickness of these films at the point where they were struck by the electron beam, was probably of the order 0.02-0.05 cm. and in exceptional cases in which oils were superimposed one upon the other, the thickness may have reached an upper limit of 0.1 cm.

Some films were too thin to show interference colours and occasionally in the case of films on copper oxide backings, the ring pattern of the oxide was obtained with the oil pattern superimposed upon it. From the penetrating power of the electron beam, these films must have been about 100 Å. in thickness. In all probability, the length of the chain carbon compounds present in the samples would be 40 Å. and might be very much more. Thus it is seen that in the case of thin films of the lubricant, conditions approaching boundary lubrication—monomolecular layers—were obtained.

The backing generally used was either a copper block about 1 cm. square polished on 0000 emery paper or a similar surface oxidised by heating. Similar blocks of lead, silver, nickel, steel and iron were also employed in the investigation of the effect of the backing upon the degree of orientation of the molecules of the lubricant.

Types of Pattern.

The various types of pattern obtained by the reflection of a beam of fast electrons from long-chain compounds have been accounted for, both theoretically and practically, by Murison. In this work it is only necessary to consider three:—

(a) Diffuse Rings or No Pattern, indicating a random arrangement of the molecules. (Figs. 1 and 2.)

(b) Diffuse Rings with one or more spots appearing on the second ring, indicating some orientation of the molecules. (Figs. 3 and 4.)

(c) A straight line pattern with spots on the lines—the "grease pattern," indicating the complete orientation of the molecules. (Fig. 5.)

Pattern (c) is given by substances such as vaseline, paraffin wax, picein, etc.: hence the term "grease pattern." If the long-chain molecules in a substance are all arranged parallel to each other and normal to the free surface, but otherwise have a random distribution, then each molecule will act as a scattering centre independent of the others, and it is seen the effects of the various molecules will be additive. From such considerations, Murison showed that the directions of maximum intensity of the radiation scattered by the carbon atoms lie on cones with the molecule as axis. If the incident radiation is almost normal to the molecules, the angles of the cones are very large for the earlier orders and the curves cut the photographic plate in straight lines. The spots on the lines (Fig. 5) are explained as due to reflection from planes formed by carbon atoms as the molecules become packed closely together. The strong side spots on the second order line of the pattern were shown by Murison to arise from the 110 plane in the hydrocarbon structure with a spacing of 4.17 Å. The

⁴ Murison, *Phil. Mag., Ser. (7)*, 1934, 17, 201.

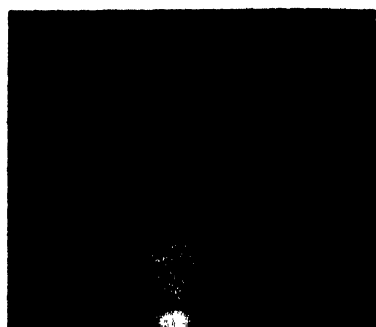


FIG. 1.



FIG. 2.

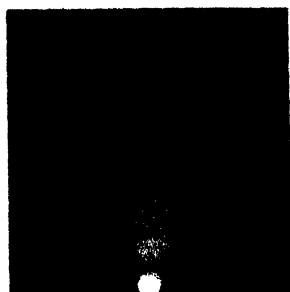


FIG. 3.

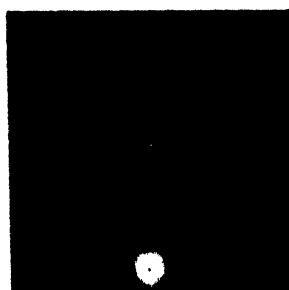


FIG. 4.

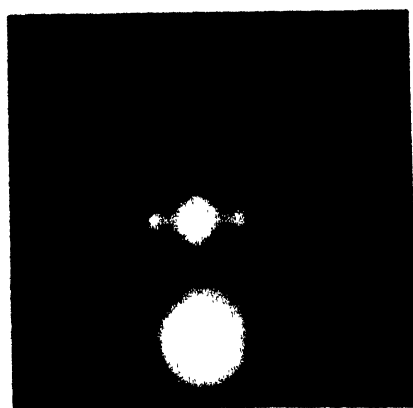


FIG. 5

(To face page 608.)

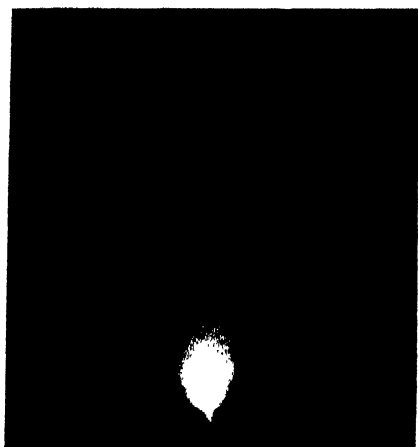


FIG. 6. - Initial chromium pattern
See page 615

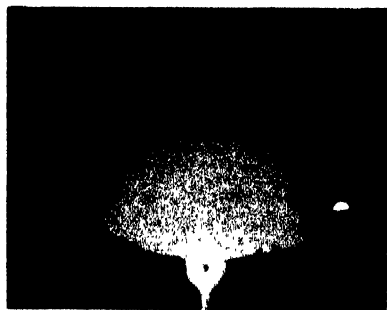


FIG. 7. -Pattern after specimen heated for
 60 hours at 250 -300 °C.
See page 615.

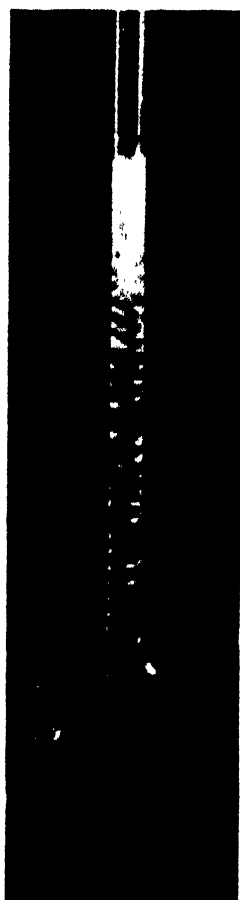


FIG. 8. - Coagulation of a
 toluene emulsion by ultra-
 sound. (About $\frac{1}{4}$ natural
 size)
See page 618.

more intense central spot, which always appears with the above side spots, is due to reflection from carbon atoms arranged in planes parallel to the surface, the distance between consecutive atoms in the molecule measured along the chain axis being 1.27 Å. The spots from these planes will lie in the plane of incidence on the even-order lines and the more regular the packing of the molecules, the more numerous will be the spots appearing and, correspondingly, the less intense will be the lines.

Pattern (b) represents an intermediate stage between the random arrangement of the molecules of pattern (a) and their complete orientation as in pattern (c). The spots which occur on the diffuse rings are the more intense ones of pattern (c). In most cases only the central spot on the second order line is obtained. It is conceivable that pattern (b) may represent a thermal equilibrium position of orientation, the molecules, impinging on the surface of the backing and becoming oriented will tend to evaporate off into the overlying fluid, if the field of force at the interface is not sufficiently strong. The number of molecules oriented in the steady state—i.e., when the number of molecules meeting the surface of the backing and becoming oriented is equal to the number of oriented molecules leaving the interface,—will depend upon the type of molecule, the fields of force at the surface and the temperature. In pattern (a), these are such as to give practically no orientation in the steady state.

Murison has suggested that, in the case of a thin film, as a result of irregularities in the surface of the backing, some parts are only a few molecules thick, and here the orientation extends to the free surface. In other places, the film is so much thicker that the orientation, beginning at the solid-liquid interface, is gradually destroyed by the heat motions before the liquid-gas interface is reached. The former region gives rise to the spots and the latter to the blurred rings.

Experimental Results.

The experiments were carried out with two sets of lubricating oils.

The first set consisted of some fourteen samples, all mineral oils except for one sample which was a vegetable oil containing 97 per cent. castor oil. Two of the mineral oils—Wakefields XXL and Aero Shell—contained about 6 per cent. fatty oil.

A number of specimens of each sample were prepared on the same type of backing and diffraction pictures obtained. This was necessary owing to the uncertainty in the thickness of the films. From the results an order of decreasing degree of orientation of molecule with the backing used could be deduced.

It is well known that many lubricants, when exposed to the air, take up oxygen and become thick—a process technically spoken of as "gumming." This change in viscosity may be scarcely appreciable when the liquid is kept in bulk, but when it is spread over a bearing as a thin film exposed to the air it may rapidly become a sticky mass and cease to lubricate.

This ready oxidation of a lubricant is a serious disadvantage, especially as the running temperature of bearings in machinery often reaches high values; thus this often becomes the crucial test for a lubricating oil.

The Electron Diffraction method provides a very sensitive test for any oxidation tendencies. It was found that specimens of many samples showed a degree of orientation of their molecules which increased with the time for which they were kept in the apparatus under a fairly high vacuum. At first, it was suspected that tap-grease vapour was condensing on the specimen in the apparatus. As tap-grease shows a "grease" pattern when prepared in thin film, if an oriented layer of the tap-grease formed on the surface of the oil under test, an increased orientation would be observed. If the tap-grease only dissolved in the oil, the tendency of the molecules of the mixture to orientate would be greater than before. This was demonstrated by experiments made to investigate the effect of adding an oil or

solid grease, etc., the molecules of which were known to orientate strongly, to a sample of lubricant showing no orientation. It was found that the presence of a very small percentage of the orienting substance was sufficient to ensure that the mixture should show strong molecular orientation independent of the thickness of the film prepared. A second possible explanation of this time effect was that some lighter constituents of the lubricants were evaporating off leaving the longer chain compounds behind. As it has been observed by Hardy³ that orientation is more pronounced the longer the molecule, due to the greater lateral adhesion between the chains, this again would account for the observed increase in orientation.

That neither of these explanations was correct was demonstrated by the fact that the phenomenon was only shown by some oil samples, whereas, were the effect due to contamination, presumably it would have been shown by specimens of the majority of the lubricants; and, again, it was found that the same changes of pattern were even more pronounced if the specimens, instead of being kept under vacuum, were stored in dust-free air for the same time. Under reduced pressure, any evaporation from the specimen would be greatly accelerated.

The most noticeable instance of this phenomenon was observed with an oil which had been obtained by a "cracking" or destructive distillation process, and which was known to oxidise readily. The diffraction photographs showed the transformation from pattern (a) or (b) to the complete grease pattern (c) within a few hours independent of the thickness of the film used. This suggests that the surface layer of the lubricant becomes oxidised, and this oxidised layer orients itself on the surface of the oil giving the pattern (c). It is conceivable that this surface layer, in the case of a thick film of an oil which oxidises strongly may be several molecules thick.

Although these observations are made under a normal vacuum in the apparatus, it must be realised that in general there is still a small quantity of air, and hence oxygen, present, accounting for the oxidation observed.

It was found also with the "cracked" oil that on keeping a thick specimen in a very high vacuum, no increase of orientation was observed over a period of some 24 hours. However, on increasing the pressure within the apparatus to atmospheric for a few hours, orientation became apparent and a complete grease pattern was obtained, showing that the very low pressure prohibited or greatly reduced the speed of any change.

In many cases it may be that the oxidation of the unsaturated hydrocarbons present in the lubricating oils proceeds in stages. Although there is some uncertainty as to whether these unsaturated compounds are open-chain, polynuclear or naphthenic, it is conceivable that, owing to the splitting of double or more complicated bonds in the oxidation process, there may be a tendency for one end of the molecule to become loaded with oxygen atoms before the other. As shown by Hardy's work on the normal paraffins and related acids and alcohols, the addition of an —OH or —COOH group to the chain produces a remarkable increase in the lubricating power of the chain compound. This was explained by Langmuir by considering the chains as rods loaded at one end with the —OH or —COOH groups; as the rods come into contact with a solid surface, those incident upon it with their loaded end first tend to adhere for a much longer period than those meeting it with their unloaded ends. In this state of dynamic equilibrium, there are far more rods adhering by their loaded ends at any instant, and it follows that the molecular orientation will be more pronounced for the acid or alcohol than for the normal paraffin.

If the unsaturated molecules in the oil become loaded at one end with oxygen atoms on exposure to the atmosphere, an increased molecular orientation, as observed in these experiments, would be expected. Thus, after slight oxidation, it may be found that certain oils will act as more efficient lubricants owing to this increased molecular orientation; but, in

³ Hardy, *Proc. Roy. Soc.*, 1923, 108A.

practice, this fact can only be exploited if the lubricant shows no further tendencies to react with atmospheric oxygen under normal running conditions. For, as the oxidation progresses, a stage will be reached when rapid polymerisation takes place with subsequent transformation of the chains into rings, and the formation of complicated gummy substances. The following experiment illustrates the above conclusions: A sample of the "cracked" oil previously mentioned was heated for 6 hours at a temperature of 200°C . in a test tube. At this stage, a thin film still showed an increasing orientation with time, showing that oxidation was by no means complete. The oil was now spread out in a thin film upon the surface of a large sheet of plate glass and kept in a warm atmosphere, free from dust, etc., for several days. The exposing of a large surface of oil to the oxygen in the air enabled further oxidation to proceed readily. At the conclusion of this treatment, a specimen prepared showed no orientation of its molecules on immediate preparation and no tendency for an increase in the degree of orientation with time.

For naphthenic compounds, it must be remembered that the series with which we are here concerned— $\text{C}_n\text{H}_{2n-10}$, for example, present in Russian oils—are very much more unsaturated than the commoner series C_nH_{2n} , etc., whose properties are well-known. It seems probable that there may be chains formed on the rings, and these may be the deciding factor in the lubricating quality of the compound. A similar process to that suggested above would eventually result in these chains being absorbed into further complicated rings by polymerisation. It is well recognised that, in general, unsaturated ring compounds are very poor lubricants, so that little molecular orientation would be expected from these gummy polymers of extremely complicated structure and high molecular weight. Such a process as this would account for the lack of molecular orientation observed when an oil is kept for a long period exposed to the atmosphere before testing it, whether its unsaturated constituents be of the open-chain or ring categories.

Analysis of Experimental Results (Table I.).

The most efficient boundary lubricants will be the oils showing a maximum degree of orientation of their molecules when prepared in thin films, and little or no further oxidation tendencies.

Amongst these we may select the mineral oils to which have been added a small percentage of fatty oil to increase their "oiliness," and also the two mineral oils specially prepared, one by Duckham, the other by the Silvertown Lubricants Limited. Both these oils are highly refined mineral oils, containing no antioxidants or dopes at all. The castor oil specimen should also be an efficient boundary lubricant owing to its property of strong molecular orientation, but its tendency to oxidise rapidly suggests that this efficiency would quickly diminish.

After the above must be classed the Russian oil group. In general, these oils, while showing only feeble orientation of their molecules, are unaffected by atmospheric oxygen, and would thus form useful lubricants for bearings which have to run for long periods unattended. The Californian and thin Pennsylvanian oils might also be included here.

The Texan oil and the "cracked" Mineral oil G, would act as very poor boundary lubricants owing to their serious gumming tendencies.

The Pennsylvanian cylinder oil is not included in the above classification, as the effect upon the orientation of the molecules of keeping a specimen of the oil was unobservable.

It was also observed that the molecular orientation of the lubricants in thin films had little relation to their respective viscosity. For example, a thin film of Aero Shell (Spec. N₄) showed less molecular orientation than the Russian oil B₂, although it was far more viscous. Oils of approximately equal viscosities also showed large discrepancies in orientating properties.

TABLE I.—EXPERIMENTAL OBSERVATIONS.

Oil.	Type.	Specific Gravity.	Molecular Orientation.	Effect of Time on Orientation.
A ₁	Mineral, Russian.	0.915	Very slight: trace of spot on second ring occasionally obtained with thin films.	Slight increase: a ring pattern (a) showed a spot (pattern b) after 3 days, but no tendency to give grease pattern on further keeping.
B ₂	Mineral, Russian.	0.910	Some orientation: spot on second ring pattern (b) obtained strongly with thin films.	Well-marked increase: after 20 days, complete grease pattern obtained. Some increase in orientation noted within 24 hours.
C ₃	Mineral, Russian.	0.905	Very slight: trace of spot on second ring occasionally obtained with thin films.	None: after 8 days, no increase in orientation observed. Oil has tendency to evaporate.
D ₂	Mineral, Russian.	0.896	No orientation at all.	None: no increase in orientation on keeping thin film specimen 6 days.
E ₃	Mineral, Californian.	0.936	No orientation at all.	No increase in orientation on keeping specimen 36 days in air. Tendency of oil to evaporate adds to the difficulty of observation.
F ₃	Mineral, Texan.	0.940	Slight: approximately one thin film specimen in three showed spot on second ring.	Very marked increase: complete grease pattern obtained on keeping specimen 7 days in air.
G ₃	Mineral, cracked.	0.916	Some orientation: majority of specimens prepared showed the spot on the second ring; some gave grease pattern.	Very marked increase: grease pattern obtained from all specimens, independent of thickness, within a few hours.
H ₃	Mineral, Pennsylvanian (thin).	0.865	No orientation at all.	Slight increase: spot obtained on second ring after 13 days but no tendency to give grease pattern on further keeping.
I ₁	Mineral, Pennsylvanian (cylinder).	0.885	Complete orientation shown by all specimens.	Unobservable as grease pattern always initially observed.
J ₁	Vegetable (97 per cent. Castor Oil). Mobiloid R.	—	Complete orientation generally shown by thin films: always some orientation obtained.	Well marked: thin film showing spot orientation (pattern b) gives a grease pattern after 3 days. Thicker film develops spot orientation from random arrangement within 6 days.
K ₂	Mineral + 6 per cent. fatty oil. Wakefield XXL.	—	Complete orientation generally shown by thin films: always some orientation obtained.	Extremely slight: spot orientation (pattern b) given by a specimen showed little tendency to improve during 21 days in air.
L ₃	Mineral, Spec. No. DTD 109 (Duckham's).	—	Some orientation: all specimens showed spot on second ring (pattern b).	None: thin film kept 27 days showed no increase in orientation of molecules. Thick film shows no orientation at all after 6 days in air.
M ₂	Mineral, Spec. No. DTD 109 (Silvertown).	—	Some orientation: all specimens gave patterns showing at least one spot on the second ring.	Slight: thicker film gave spot on second ring on keeping 6 days, but no further improvement after another 8 days in air.
N ₂	Mineral + 6 per cent. fatty oil. Aero shell.	—	Slight: about half the specimens gave patterns showing spot on second ring. Thick films gave little orientation at all. Oil has tendency to evaporate.	Marked increase: thin film specimen giving pattern showing spot on second ring, showed complete orientation after 14 days in air.

With one or two exceptions, the results of the investigation of the lubricating properties of this set of oils are in good agreement with the results obtained in practice. In practice the oil E_2 was found to oxidise more seriously than the members of the Russian group. In the Electron Diffraction analysis, no oxidation of E_2 was observed, although its tendency to evaporate may have masked the observation of an increased orientation with time.

The second set of samples which were mainly commercial products, was found far inferior to the first set as regards orientation of molecules. However, the main conclusions drawn from the previous observations were further supported. One specimen, a motor oil of unknown origin which had proved unsatisfactory in practice, was found to show a very marked increase in molecular orientation on keeping. This oxidation was probably the cause of its inefficiency. Two specimens of Mobiloil BB (not clearosol treated) were tested. One was an unused sample, the other a sample which had been employed in a friction machine for 50 hours, during which period it had been oxidised by air at 160°C . The former showed an increasing orientation with time, the latter not so, supporting the earlier observations, since in all probability the used sample was completely oxidised after the above treatment.

Once again the agreement between the Electron Diffraction analysis and the results obtained by friction machine tests was very good. It is found easy to pick out the inefficient lubricants by the Electron Diffraction method, but, owing to its entirely qualitative nature, very difficult to differentiate between specimens which are approximately of equal efficiency.

Presence of Wax.

The addition of a very small quantity of a strongly orientating substance to a mineral lubricating oil was found to result in a mixture which always showed far stronger molecular orientation than did the lubricating oil alone. It was found that on adding a film of oil which showed no molecular orientation to a film or layer of grease showing complete orientation, the oil took up the grease and formed, in general, a homogeneous liquid mixture, which still showed strong molecular orientation. This was found to be so independent of the amount of liquid oil which was added to the grease, as previously explained.

In particular, it was found that the addition of a very small quantity of paraffin wax to a lubricating oil resulted in a marked increase in the resulting molecular orientation. This fact suggested that the molecular orientation of oils known to contain paraffin waxes, was due to the wax content. To test this view, two samples of oil were obtained, one of which was known to contain a very small percentage of paraffin wax, and the other the same oil with the wax removed by treatment with acetone. It was found that spot orientation (pattern *b*) could be obtained with the first when spread in a thin film on appropriate backings, but that no orientation at all could be obtained from the specimen from which the wax had been removed. These experiments seem to confirm the above conclusion.

Discussion.

The constituents of the lubricating fractions of mineral oils consist chiefly of compounds of the general formulæ C_nH_{2n-2} to C_nH_{2n-4} . Of the above hydrocarbons, those of the general formula C_nH_{2n-4} are recognised as giving the lowest coefficient of friction as well as the greatest durability. This is illustrated to some extent in the case of the two Pennsylvanian oil samples tested. The heavier oil, which contains a greater proportion of compounds of the general formulæ C_nH_{2n-4} and C_nH_{2n-6} , was found much superior as regards molecular orientation to the lighter oil, the chief constituents of which are compounds of the general formulæ C_nH_{2n-6} and C_nH_{2n-8} .

The Texan petroleum (density 0.94-0.96) are, in general, more unsaturated than the Russian petroleum, due to the presence of compounds of the general formula C_nH_{2n-12} . Such compounds would be expected to possess great chemical activity. Prolonged reaction with atmospheric oxygen results in the formation of oxidation products which are, in general, gummy substances and useless for lubricating purposes. Such an oxidation was actually observed with the specimen of Texan oil under test.

The effect of the addition of a small percentage (2 per cent.) of oleic acid to a mineral lubricating oil seemed to be to reduce slightly the rate of increase of molecular orientation on keeping the specimen in air.

The explanation of the occasional lack of agreement between the results obtained in the present investigation and in practice, may be in the fact that the oils are tested under rather different conditions of temperature in the two cases. In modern machinery, under boundary lubrication conditions, the temperature of the bearing is often 100° - 150° C., and may be higher, whereas, in the electron diffraction experiments the tests are carried out at room temperatures.

Effect of the Backing.

The frictional resistance of a bearing is due to what may be termed the 'unctuous' nature of its surface; for each metal tested for slipperiness against itself, without any lubricant, gives a distinctive coefficient of static or boundary friction.

In order to test whether the backing upon which an oil film was prepared influenced in any way the degree of orientation of the molecules, a number of blocks of different substances, mainly metals, was used. All the blocks were polished on 000 emery, and in every case a thin film of the same mineral lubricating oil was used as giving the most instructive indication of the orientation on the metal surface. For, in the case of an oil or grease whose molecules orientate readily, a "grease" pattern is obtained by electron diffraction independent of the backing used. On the other hand, with oil specimens which in thin films show a spot on the second ring (as did the mineral oil used in this investigation), the effect of the backing can be investigated, since, as the orientation at the oil-air interface is slight compared with that at the metal-oil interface, the possibility of the orientation of the molecules persisting to the free surface depends almost entirely upon the degree of orientation at the metal-oil interface.

TABLE II.

<i>Backing Used.</i>	<i>Experimental Observation (thin film of lubricant).</i>
Clean copper.	No orientation.
Oxidised copper (Cu_2O).	No orientation.
Steel.	Orientation (spot on second ring).
Tarnished steel.	No orientation.
Swedish iron.	Slight orientation (spot on second ring).
Slightly oxidised, Swedish iron (α - Fe_2O_3).	Orientation (spot on second ring).
Nickel.	No orientation.
Lead.	No orientation.
German silver.	Slight orientation (spot on second ring).

Thus from the results shown in Table II., it is observed that iron, steel and german silver are the more suitable for use with the mineral oil lubricant in question than the other materials tried: thus iron, steel and german silver are the more "unctuous".

Experiments with pure substances as lubricants have shown that the more "unctuous" the metal forming a bearing, the lower will be the friction obtained with any particular lubricant. Thus iron, steel and german silver should be efficient bearing materials. In practice the best materials are mild steel, cast iron, and the white metals.

Corrosion of Metals by Oils.

A number of experiments were carried out upon the corrosion of metals by oils, an attempt being made to identify the nature of the corrosion products by Electron Diffraction.

In this investigation, the procedure was to immerse a metal surface polished on 000 emery completely in the oil to be tested in a test tube. The whole was then heated in an electric furnace to a temperature of about 250° C., the state of the surface being investigated by inserting the specimen in the apparatus after, say, $\frac{1}{4}$ hour, 3 hours, and 12 hours. Prior to the insertion of the metal, the furnace was switched off and the whole allowed to cool to room temperature. The metal block was then removed, washed in benzene and ether to remove any residual oil on the surface, and an electron-diffraction picture taken. In this way, provided an initial picture is taken of the metal surface before the commencement of the experiment, the gradual contamination of the surface can be investigated.

A number of different metals, including copper, chromium, nickel, iron and steel were used both with a mineral and a fatty oil. It was found that after a period of 15-30 minutes heating in the oil at 250°-300° C., the initial ring pattern of the polycrystalline metal gave place to a new sharp ring pattern either of the oxide alone, or of the oxide and the metal. In the case of iron, the new pattern was of α -ferric oxide (α -Fe₂O₃), while for nickel and chromium, rings of both oxide and metal were generally present. Copper showed a pattern of cuprous oxide (Cu₂O) when the metal was heated in the vegetable olive oil, but an unidentifiable pattern when heated in a mineral oil. This substance, which was not cupric oxide, nor the third copper oxide discovered by Thomson and reinvestigated by Murison, had the following set of spacings:

$$\begin{array}{llll} 3.28 \text{ W} : & 2.41 \text{ W} : & 1.92 \text{ S} : & 1.67 \text{ S} : \\ & & (\text{unresolved doublet}). & \\ 1.26 \text{ S} : & 1.12 \text{ W} : & 0.96 \text{ M} & \end{array}$$

There is little likelihood of there being any copper rings present as the strong $\sqrt{3}$ ring, with a spacing of 2.11, does not appear.

There was difficulty also in identifying the new pattern obtained with steel heated in a mineral oil. The patterns obtained in this case were poor and indistinct, due to much background scattering. In all probability, the pattern was due to oxides and metal together.

As in many cases the patterns of both the metal and the oxide appear, the layer of oxide must definitely be less than 10⁻⁴ cm. thick.

On further heating the specimen in the oil and re-investigation of the surface by electron diffraction photographs, it was found that there was no further change in the ring pattern, but the background intensity increased until after a period varying from 5-10 hours for different metals, only the strongest rings of the initial pattern remained visible.

It was found that if the metal was heated in the oil for much longer periods—50-60 hours for example—the sharp ring pattern was completely suppressed and diffuse rings appeared on the plate, showing a random arrangement of molecules of impurity, greater than 10⁻⁴ cm. in thickness, present upon the surface. If the specimen was now kept in benzene for several days, it was found that the diffuse ring pattern disappeared and the original sharp rings began to appear in the still intense background. Fig. 6 shows the initial pattern for a chromium surface and Fig. 7 the new pattern after 60 hours' heating.

Thus from these experiments we can conclude that the main cause of corrosion is the accumulation of an amorphous layer, probably of some organic substance, upon the surface of the metal. The corrosion was found to be more serious for an oil which had been used for a long period before this experiment was carried out than for the same oil previously unused. This suggests that the organic compound concerned may be some gummy

oxidation product. No marked difference was observed in the behaviour of the mineral and vegetable oils in this respect. Of the metals, chromium and nickel, in general, seemed to suffer less seriously from the corrosion effect than did the iron and steel.

Summary.

An electron diffraction method for investigating the molecular orientation and hence the boundary lubricating properties of lubricating oils is described. The results obtained are found to be in reasonable agreement with those actually obtained in practice. In the process of the experiments, some of the commoner defects of lubricants, such as oxidation and corrosion, are also investigated.

In conclusion I would like to express my gratitude to Professor G. P. Thomson for suggesting the research, and for his kindly interest and encouragement during its progress.

THE MECHANISM OF COAGULATION BY ULTRASONIC WAVES.

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1.

When emulsions are produced by ultrasonics, their concentration quickly reaches a limiting value.¹ This cannot be explained by spontaneous coagulation going on in these emulsions, since it is too slow; ¹ one is dealing with a specific coagulating action of the ultrasonics.

This coagulation is not due simply to the strong movement of the liquid when irradiated, though such an action has to be taken into account to a certain extent,² for unprotected emulsions of mercury or toluene are markedly destroyed by vehement shaking.

The following experiments show that the existence of a limiting value must be attributed to a special mechanism of coagulation; it is the interaction between the emulsifying and coagulating action of the ultrasonics which is responsible for the final concentration of the emulsion.

Since the fundamental difference between the mechanism of emulsification of mercury and that of organic liquids ("oils"),³ becomes again apparent, they may be treated separately.

2.

In mercury emulsions the coagulation effect may readily be separated from that of emulsification: two test tubes containing 0.5 c.c. Hg + 5 c.c. H₂O are irradiated till the limiting value is reached (thirty seconds and 115 mA., as strength of the current entering the secondary circuit).¹ In the one tube the aqueous emulsion is separated from the bulk of mercury and irradiated again for thirty seconds; the macroscopic movement of the

¹ C. Bondy and K. Söllner, *Trans. Faraday Soc.*, 1936, **32**, 556.

² Cf. e.g. A. Boutaric and J. Bouchard, *Bull. Chim. Soc. France*, (4), 1932, **81**, 543; cf. *Zentralblatt*, 1932, **II**, 2024.

³ C. Bondy and K. Söllner, *Trans. Faraday Soc.*, 1935, **31**, 835, 843.

liquid was not nearly so strong as when the latter was shaken vehemently. As soon as the coarse particles had settled (two minutes after the irradiation was stopped), the concentration of each emulsion was determined: the one which was irradiated a second time was transparent, light grey and contained only 0.8 g. Hg per litre; the other was opaque, black and contained 5.9 g. Hg per litre.

Coagulation by ultrasonics proceeds in the aqueous phase. Emulsification, however, as has been shown,⁴ proceeds in the surface of the bulk of the mercury, where thin films of the metal are lifted up and dispersed. Hence the amount of Hg must be sufficiently large if emulsification is to be observed at all.

The limiting value of concentration—using high energies (100 mA. and more)—is 6 g. Hg per litre, *i.e.* 30 mg. in 5 c.c. and is reached after thirty seconds irradiation. If small amounts of Hg of this order of magnitude (2 to 30 mg.) are added to 5 c.c. H₂O and irradiated for thirty seconds or even much longer, practically no emulsification is observed; the aqueous phase is just slightly turbid, the opacity increasing with the amount of mercury used. Strong emulsification does not occur till 100 mg. and more of mercury are added; the emulsions are then opaque and greyish black, although less dense than those prepared in the presence of larger amounts of mercury. If small amounts of Hg (5 to 50 mg.) are added to a concentrated emulsion, which has been separated from the bulk of the metal, and these systems are irradiated under the conditions mentioned above, then the emulsions are coagulated practically as strongly as in absence of mercury in bulk.

Coagulation depends upon the volume of the aqueous phase: less mercury is coagulated, if the volume of the aqueous phase is smaller. If a given amount of Hg is irradiated in 1 c.c. H₂O instead of 5 c.c., the emulsion becomes more concentrated.⁴

We must therefore distinguish between the locus of emulsification, a thin layer *s* at the interface between mercury and water, lying mainly in the interior of the bulk of the metal,⁴ and the locus where only coagulation and no emulsification takes place, *i.e.* the aqueous phase of the emulsion *l*. With increasing *s* the average concentration of the emulsion increases, with increasing *l* it decreases.⁵

3.

Emulsions of toluene (and other oils) seem at first to behave quite differently. If such an emulsion (produced by ultrasonics) is separated from the bulk of toluene, and then irradiated once more for thirty seconds (or even much longer) under the same conditions, no coagulation takes place; the emulsion has exactly the same properties as one prepared by a single irradiation. This difference in behaviour between "oil" and mercury emulsions is readily understood, when it is remembered that the mechanism of emulsification is quite different with "oils."—Here emulsification is caused by cavitations occurring at the interface of the two liquids, and there is no need for coherent masses, as with mercury, so that any small amount of toluene may be emulsified, as is proved by the following experiments.

⁴ W. T. Richards, *J. Am. Chem. Soc.*, 1929, 51, 1724; C. Bondy and K. Söllner, *loc. cit.*, p. 843.

⁵ *s* does not necessarily increase indefinitely with an increasing quantity of mercury. On the one hand too large a metal mass may damp the vibrations; on the other hand only those parts of the metal act as *s* where the water is driven into it, *i.e.* mainly a ring-shaped zone round the meniscus. Cf. ⁴ and H. B. Bull and K. Söllner, *Koll. Z.*, 1932, 60, 263.

As mentioned in a previous paper, 4 per cent. toluene (this being the limiting value) are emulsified in less than thirty seconds using an energy corresponding to 115 mA., i.e. 0.2 c.c. toluene in 5 c.c. H_2O . If different amounts of toluene (between 0.05 and 0.6 c.c.) plus 5 c.c. H_2O are irradiated with 115 mA. emulsification sets in directly; after thirty seconds the samples containing 0.2 c.c. and more of toluene are equally opaque; in those containing smaller amounts opacity decreases proportionally to the amount added. With 0.2 c.c. toluene and less no external phase (or large drops) are observed, after irradiation, as is the case with more than 0.2 c.c. toluene.* This behaviour remains the same, irrespectively of whether the liquid wets the walls of the tube. The result is substantially the same, if water is emulsified in toluene.

Under the conditions of these experiments (a few c.c.s of liquid, normal test tubes and high energies) the locus of emulsification and coagulation are identical. In order to separate them, one must change either the shape of the vessel or the energy applied.

If instead of ordinary test tubes, in which the liquid is almost entirely surrounded by the vibrating oil fountain, a long tube (e.g. 50 cm. long, 1 cm. wide) is used, coagulation may readily be observed: the tube is filled with a 4 per cent. toluene emulsion up to a height of 35 cm. and is dipped with its lower end into the oil fountain (energy 115 mA.). Almost immediately more or less regular, more pronouncedly whitish zones appear in the lower and middle part of the tube (Fig. 1).⁷ In these zones the droplets of the emulsion are accumulated. They soon form larger drops which may be seen rising to the surface, if the tube is taken out of the fountain for a moment. During irradiation these larger drops are, at first, retained at the level of their formation. Shortly afterwards on growing larger they jump from one zone to the next, thus forming gradually a coherent layer of toluene on the top of the liquid. In the ranges lying between these zones of accumulation the concentration of toluene is markedly reduced. If the irradiation is extended for some minutes, the liquid in the lower and middle part of the tube becomes transparent, containing only small amounts of toluene. But the top part of the liquid to a range of 10 to 15 cm. never becomes quite clear, this range, of course, being smaller at lower energies (Fig. 1) close to the always violently moving interface water/toluene there is always a dense emulsion.

If the same experiment is done with water filling the tube to a height of 35 cm. and covered with a few drops or c.c.s of toluene, emulsification at once takes place close to the strongly agitated interface; below the latter to a range of several cms. the aqueous phase contains large amounts of dispersed toluene, the concentration being practically zero 10 or 15 cm. below the interface water/toluene. In both experiments the final stationary state after prolonged irradiation is identical.

Substantially the same results are obtained with an organic liquid heavier than water; e.g. in an emulsion of nitrobenzene zones of accumulation occur in the lower and middle part of the tube, (leading to a rapid decrease of concentration in these parts, which is much slower near the violently moving surface), and a range of emulsification close to the interface nitrobenzene/water at the bottom. If a few c.c.s of nitrobenzene are covered with a tall column of water, again emulsification takes place only close to the interface. If some nitrobenzene is brought on the top of a tall column of water, the latter being irradiated, the nitrobenzene is first

* Of course primary emulsification is quicker with more toluene up to a certain limit. There is a larger interface, where initial cavitation may occur. Nevertheless, with high energy as well as with small amounts of toluene the stationary state is reached in thirty seconds.—When once emulsified, the presence or absence of a surplus of "oil" has no importance at all.

⁷ To obtain a better photograph a column of emulsion only about 14 cm. high was used here, and correspondingly a somewhat lower energy was applied. The oil fountain is to be seen at the bottom.

emulsified close to the surface water/air; emulsification stops almost entirely whilst the organic liquid is sinking through the middle part of the tube, but takes place again, as soon as the nitro-benzene reaches the bottom, where it dips into the fountain.

In this way it was possible, though not very completely, to separate the locus of coagulation from that of emulsification. Where zones of accumulation appear coagulation occurs; where their formation is prevented by vehement movement of the liquid, emulsification and coagulation counterbalance each other. Movement is specially strong close to a surface or to an interface between two liquids; it is adversely affected by too small an amount of the second liquid. Thus very favourable conditions for emulsification prevail, when the more usual test tubes and amounts of liquids are utilised.

It is obviously not the amount of energy entering the system which is decisive for the different behaviour in the locus of coagulation and that of emulsification. The main point is that zones of accumulation can be produced.

This phenomenon becomes the more conspicuous, also in short columns of liquid, if narrower tubes are used; in narrow tubes the effects of stirring and of eddies are strongly reduced. These effects are due, at the bottom of the tube, to an irregular admission of the energy transferred from the oil fountain, quite generally to irregularities of refraction and reflexion at walls and surfaces. Close to the latter such irregularities prevent the formation of well-defined, constant stationary waves, which produce the visible accumulation.

These stationary waves in the liquid are obviously the cause of the accumulation of droplets, a phenomenon identical with Kundt's dust figures.⁶ In such a zone coagulation takes place, in part owing to the much higher concentration, in part owing to a kind of ortho-kinetic coagulation:⁶ drops of different size moving with different velocity, thus colliding and coalescing.

These results may be confirmed by experiments with low energy. If a long tube containing a column, 30 to 35 cm. high, of a 4 per cent. toluene emulsion is dipped into an oil fountain of 40 to 50 mA., zones of accumulation appear soon, large drops are formed and rise up to the surface, and after a few minutes the aqueous phase is covered with a coherent layer of toluene. This experiment is distinguished from the one performed with higher energy only in so far as the whole process occurs much more slowly and as the zone of coagulation extends practically up to the surface, the latter being only weakly agitated. If a tall column of water covered with a layer of toluene is treated with ultrasonics of the same low energy, very slight changes occur after an irradiation of several minutes: the thin layer of water between the toluene and the glass, initially covering the glass

⁶ It has long been known that suspended particles are driven together by stationary sound waves. (Cf. A. Kundt and O. Lehmann, *Ann. Physik* (Poggendorff), (1874), 153, 1; K. Döring, *Ann. Physik*, (IV.), 1908, 25, 227.) Boyle and co-workers (cf. e.g. R. W. Boyle, *Science Progress*, 1928, 23, 75) have described this phenomenon with ultrasonics. A flocculation of solid particles was mentioned by R. W. Wood and A. L. Loomis (*Phil. Mag.*, (7), 1927, 4, 417) the coagulated material being driven to the surface by "radiation pressure."

N. Marinenco (*C.R.*, 1932, 194, 1824) shortly describes a similar effect due to stationary waves, after E. Newton Harvey (*Biol. Bull.*, 1931, 59, 300), had described the same for gas bubbles. A first account of our own work on this subject was given by H. Freundlich (*Technical Aspects of Emulsions*, p. 1, London, 1935).

⁷ P. Tuorila, *Kolloidchem. Beihefte*, 1927, 24, 1, 27; G. Wiegner, *J. Soc. Chem. Indust.*, 1931, 50, 55.

surface, is emulsified in the toluene and a water layer just below the interface of the two liquids becomes also slightly turbid.

By reducing the energy still further, zones of accumulation may also be produced in short columns of liquid contained in normal test tubes,¹⁰ and energy ranges may here also be readily found where upon irradiating, coagulation occurs but no emulsification.

The energy of ultrasonics must exceed a certain value in order to have an emulsifying effect upon mixtures of organic liquids and water. Below this limiting value weak ultrasonics only have a coagulating effect on oil emulsions. Thus the coagulating action may be isolated. When using high energies dispersion and coagulation cannot be separated from each other close to surfaces or interfaces, where the movement is too vehement, since cavitation is obviously favoured here, thus increasing the movement still more and making it more irregular. Coagulation may become visible in the interior of the liquid, where fairly constant zones of accumulation can be formed. In the ranges close to surfaces and interfaces, however, coagulation also proceeds, zones of accumulation being produced irregularly as to space and time; the same forces act here upon the particles as in other cases but the high local concentrations so favourable for coagulation are not attained.

All this may be confirmed by a third method of separating coagulation from emulsification. If an emulsion in a long tube is covered with a tall column of a liquid of smaller specific gravity and an external pressure is applied by means of compressed gas, cavitation, and therefore emulsification is prevented, whilst coagulation still proceeds. This latter process is again favoured by the formation of stable zones of accumulation, i.e. high concentration.

In these zones, furthermore, the coagulated material is retained, since it cannot cream up or settle down, thus forming excellent centres of coagulation for other smaller droplets. If more or less regular and stable stationary wave patterns are not formed, the coagulated material creams readily up or settles down or is, as a rule, driven to the surface by "radiation pressure."¹¹

Now it may easily be understood that the coagulation by ultrasonics of mercury emulsions is not essentially different from that of oil emulsions; it is only somewhat simpler, the disturbing effect of cavitation being excluded. If a long tube containing a mercury emulsion is dipped into the oil fountain, regular striations of mercury soon appear on the walls of the tube, provided that the latter is lying in a position about horizontal.

As was to be expected, with mercury emulsions the disturbing influence of surfaces is not nearly so distinct: firstly cavitation cannot bring about re-emulsification of already coalesced mercury suspended in the liquid; secondly the coagulated material settles down somewhat quickly, being too heavy to be kept in suspension in the liquid by stationary waves.

Ultrasonics cause coagulation in suspensions just as in emulsions. The analogy is so obvious that it hardly needs a separate treatment. It can be shown very impressively when irradiating a very unstable suspension (e.g. that of quartz in some organic liquids). When irradiated under suitable conditions the dispersed phase is coagulated at once.

¹⁰ This readily explains why, with low energies, low maximum concentrations are found. Cf. C. Bondy and K. Söllner, *loc. cit.*, p. 556, Table II. (a).

¹¹ Cf. e.g. W. R. Wood and A. L. Loomis, *loc. cit.* ⁹.

4.

Clear stationary wave patterns produced by ultrasonics in a liquid may be investigated most successfully with the following device: the emulsion (or suspension) is filled into a thick-walled capillary which is slightly U-shaped in the middle; this part is dipped into the oil fountain, the two ends protruding horizontally sideways (Fig. 2). Thus one may avoid the very disturbing strong changes in concentration due to creaming up or settling down close to the meniscus. If high energies are to be applied, it is advisable to make the U-shaped part in the middle out of a thin-walled glass tube, so that more energy may be transmitted to the liquid. As the liquid may be thrown out when irradiated and as the striations are disturbed by too vehement a movement of the meniscus, the opening of the capillary may suitably be stopped with piceine, leaving a short air gap as buffer between the stopper and the meniscus. As dissolved gases are always partially driven out from saturated solutions,¹² it is advisable to use liquids which are not fully saturated with gas, since otherwise gas bubbles are formed, which, by jumping from one node to the next, disturb the regular arrangement of the striations or, if large, interrupt the sound transmitting column of liquid.

Such a capillary, then, is filled with an aqueous emulsion of benzene, toluene, etc., and irradiated. The stationary waves cause immediately or, with low energy, in the course of some seconds the formation of Kundt's dust figures (Fig. 3A). With increasing time of irradiation the zones of accumulation become much sharper. Under favourable conditions thin disks with a well-defined boundary seem to stand upright in the liquid. The distance between two stripes is $\lambda/2$, λ being the wave-length calculated from the frequency and the sound-velocity in the liquid. The first stripe is found at a distance of $\lambda/4$ from the meniscus (cf. Fig. 3A), i.e. at a node, the meniscus always being the locus of an antinode.

If exactly the same experiment is done with emulsions of nitrobenzene or mercury, or with a suspension of quartz, the first stripe lies at the meniscus itself, the next at a distance of $\lambda/2$ from the meniscus, i.e. at the antinodes (cf. Fig. 3B). So far as these experiments have proceeded, accumulation in aqueous systems occurs at the nodes if the dispersed substance is less dense than water; and at the antinodes if it is denser than water or the aqueous solution used. The mechanism of accumulation and coagulation is obviously the same in both cases.

This phenomenon is remarkable from a theoretical point of view,¹³ but as it does not so much concern the coagulation of emulsions, it need not be discussed here in detail.¹⁴ The following experiment, however, deserves mention; in an aqueous system containing particles both denser and less dense than water, ultrasonics may separate the two kinds of particles from each other. This is shown in Fig. 3C for a mixture of an emulsion of toluene and a suspension of quartz; this figure is evidently produced by a superposition of Figs. 3A and 3B. Stripes of toluene and of quartz alternate with each other, the distance between a stripe of the one and the

¹² Cf. e.g. E. Newton Harvey, *loc. cit.* ⁸, R. W. Wood and A. L. Loomis, *loc. cit.* ⁹, and W. T. Richards and A. L. Loomis, *J. Am. Chem. Soc.*, 1927, **49**, 3086.

¹³ Cf. e.g. L. V. King, *Proc. Roy. Soc.*, 1934, **147A**, 212.

¹⁴ One may assume that the decisive factor is not the differences in specific gravities; it may be some closely related function, which takes into account also the different sound velocities. (Cf. preferably the work of R. W. Boyle and co-workers: R. W. Boyle, *Nature*, 1928, **121**, 55; *Science Progress*, 1928, **23**, 75; R. W. Boyle and D. K. Froman, *Canad. J. Res.*, 1929, **1**, 405; R. W. Boyle and T. F. Lehmann, *Physic. Rev.*, (2), 1926, **27**, 518; *Trans. Roy. Soc. Canada*, (3), 1927, **21**, 115; *Canad. J. Res.*, 1930, **3**, 491, and other papers).—For the formation of the stationary wave patterns the viscosity of the medium of dispersion and vortex motion in the latter seem to play a rôle, which can hardly be altogether neglected. Cf. E. N. da C. Andrade, *Science Progress*, 1932, **27**, I., 73.

other being $\lambda/4$. Toluene and quartz are readily distinguished by the fact that the former creams up, the latter settles down.¹⁶

These results also prove definitely that we are dealing with stationary waves in the liquid itself. It is possible to calculate the sound velocity in the liquid correctly from the known frequency of the waves and the wavelength determined from the distance between the stripes.

The accumulation of dispersed substance at the nodes or antinodes is strongly influenced by the size of the particles, as is shown by the following experiments: three capillaries having the same dimensions were filled with suspensions of quartz (concentration about 3 per cent.). The quartz powder had been roughly fractionated. The capillaries contained particles with diameters between 4 and 10 μ , 1 and 4 μ , and below 1 μ respectively. On irradiating with medium energy the wave patterns are formed immediately with the largest particles, the liquid between them being free from particles; with the particles of medium size it takes a few seconds for the space between the striations to become practically free of particles, many seconds for the striations to become somewhat narrow and a still longer time until the pattern looks like that in the first capillary. In the third tube zones of diminished concentration appear after several seconds, zones of a certain accumulation are to be seen after a minute, but even after thirty minutes the whole pattern is blurred. In suspensions containing particles of some tenths of a μ the effect is still less distinct. In truly colloidal solutions with our wave-length, they have so far not been obtained at all. But if by coagulation with electrolytes large secondary particles are formed, the latter may be accumulated on irradiation.

The forces—one may call them "radiation pressure"—due to the diffraction of sound energy¹⁶ by the individual particles must be considered to be the ultimate reason for the coagulation by ultrasonics. These forces invariably cause a kind of ortho-kinetic coagulation and, when stationary waves occur, build up the zones of accumulation, which for several reasons (those we already know are mentioned above) so decidedly favour coagulation.

The coagulation process was investigated under the microscope using a somewhat wider capillary. Freshly prepared oil and mercury emulsions are markedly heterodisperse. On irradiation the coarser particles are rapidly accumulated at the nodes or antinodes; the smaller particles need a much longer time. One observes how the coarser particles are accumulated in a short time, coalescing into one or several drops more or less rapidly; if irradiation goes on, the liquid between becomes clear and the large drops increase in size until they contain practically the whole of the disperse phase. Figure 4a shows this phenomenon with a toluene emulsion some minutes after irradiation was started with medium energy.¹⁷ Fig. 4b after prolonged irradiation.¹⁸ Substantially the same may be seen with emulsions of nitrobenzene, or other oils as well as with mercury.

The behaviour of protected emulsions depends upon their concentration and degree of stability. When weakly protected, the droplets quickly

¹⁶ To show this, the photographs 3 A, B, C were taken horizontally from the side, shortly after irradiation was started with pretty low energy. The internal diameter of the capillaries was about 1 mm.

¹⁷ One is dealing here with a problem somehow similar to the problem of the scattering of light by colloidal particles.

¹⁸ As the toluene creams up, this photograph was taken from above. To get a better photograph a capillary with an internal diameter of about 3 mm. was used. Already here the striations are less regular than in Fig. 3 A, B, C.

¹⁹ The size of the drops in Fig. 4b is due to the fact that during the prolonged irradiation "radiation pressure" has driven large drops of coagulated toluene to the end of the column of liquid, where they are retained at the nodes, uniting with the drops already present there. Accidentally, this photograph was taken from a 3 mm. tube with thinner walls.

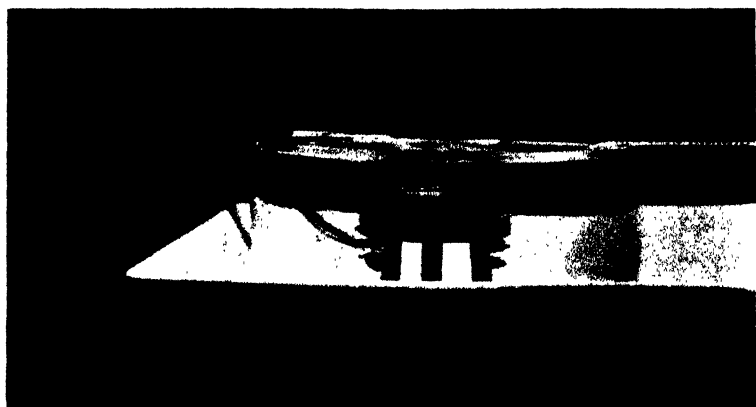


FIG. 2 Arrangement for the study of stationary wave-patterns. (About 1/2 natural size.)

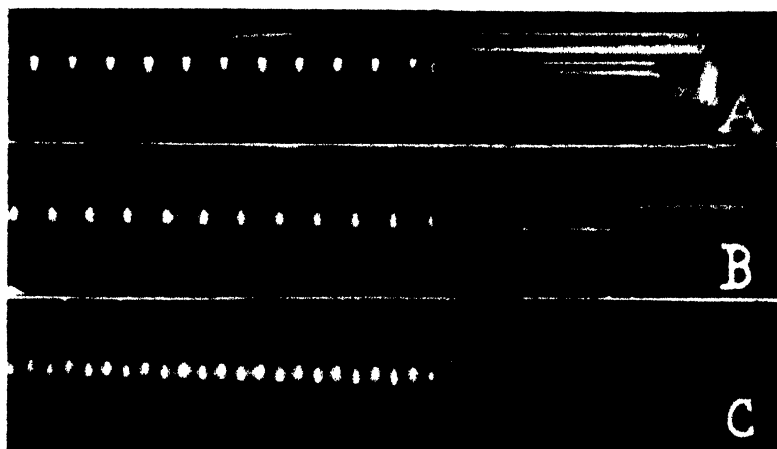


FIG. 3 Stationary wave-patterns. (About 1/5 natural size.)

- A. Toluene in water
- B. Quartz in water
- C. Toluene + quartz in water

[See page 621.]

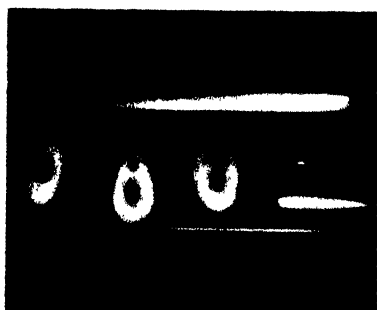


FIG. 4a.

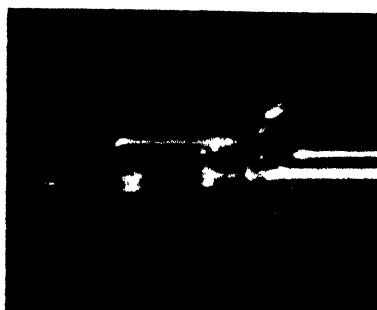


FIG. 4b

The formation of large oil drops in the individual zones of accumulation.

[To face page 622.]

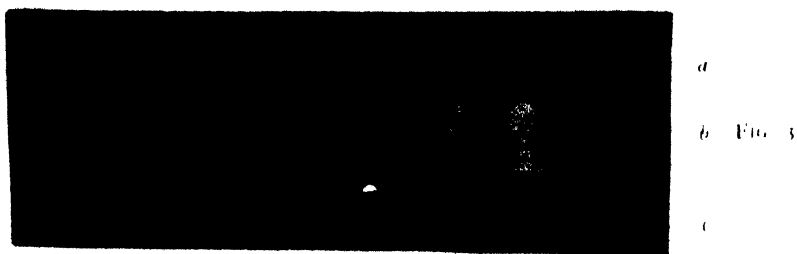
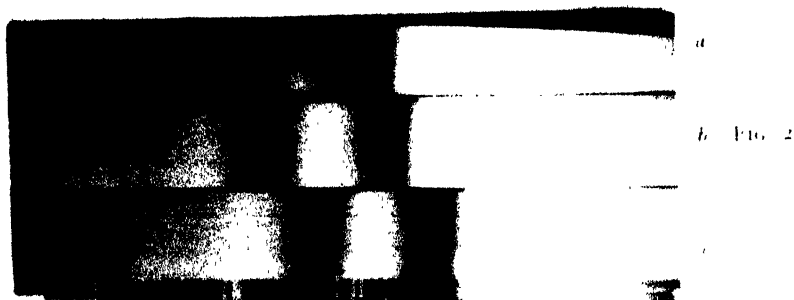
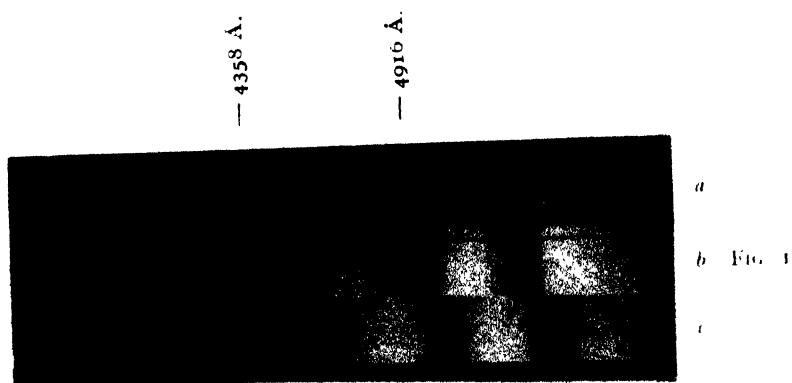


FIG. 1. - Absorption spectrum of naphthalene
 FIG. 2. - Absorption spectrum of perylene
 FIG. 3. - Fluorescence spectrum of perylene
 (a), (b), (c) refer to solutions in C_2H_5OH , C_6H_6 and CS_2 respectively
 See pages 601 and 603

increase in size on irradiation. Strongly protected emulsions behave like suspensions: the particles are only accumulated; when irradiation stops, they are dispersed spontaneously or on shaking.

Summary.

1. Ultrasonic waves display a strong coagulation action in emulsions and suspensions.

"Radiation pressure" caused by diffraction of sound energy by the individual particles drives the latter to and fro, thus increasing the rate of spontaneous coagulation by a kind of orthokinetic coagulation. It accumulates the particles at the nodes (or antinodes), wherever stationary waves occur. Here rapid coagulation sets in, the orthokinetic (and spontaneous) coagulation being enormously accelerated by the high concentration at the nodal (or antinodal) zones of accumulation, the rate of coagulation by ultrasonics being mainly dependent upon the formation of the latter.

2. In aqueous mercury emulsions the locus of coagulation may be readily separated from that of emulsification: coagulation proceeding in the interior of the aqueous phase, emulsification exclusively at the interface of large bulks of metal and water.

3. In aqueous emulsions of organic liquids this separation is not so easily effected. Both coagulations and emulsification (the latter caused by cavitations), take place. At high energies close to surface and interfaces coagulation and emulsification counterbalance each other and cannot be separated. But in the interior of the liquid under suitable conditions stationary waves and zones of accumulation (and coagulation) may be observed. Emulsification needs an energy exceeding a certain limit; coagulation may therefore be called forth exclusively below this limit, as well as by preventing cavitation (and therefore emulsification) if an sufficiently high external pressure is applied.

4. Coagulation by ultrasonics in unstable suspensions is due to the same causes as in emulsions, the analogy between the two cases being very complete.

5. The rate of accumulation at nodes (or antinodes) depends strongly on the particle-size. With the wave-lengths used, it proceeds markedly and rapidly with particles having a diameter above $1\ \mu$. Accumulation and coagulation are practically not observed with particles of truly colloidal size.

6. In aqueous systems, particles less dense than the medium of dispersion are accumulated at the nodes, denser ones at the antinodes. Thus in a system containing particles denser and less dense than the medium of dispersion the particles of different density may be separated from each other by irradiation with ultrasonics.

Our heartiest thanks are due to Professor H. Freundlich for his very helpful criticism and advice during this work. We are also greatly indebted to Professor F. G. Donnan, F.R.S., for his generous hospitality and his interest.

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THE PHOTO-ELECTRIC MEASUREMENT OF THE ABSORPTION OF SODIUM RESONANCE RADIATION.

BY FRED FAIRBROTHER AND JAMES L. TUCK.

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This paper is primarily an account of an investigation into the possibilities of the measurement, by a photo-electric method, of the absorption of resonance light by a metal vapour: we have applied the method so far only to the absorption of sodium resonance light, but the general method is applicable also to other metal vapours whose resonance radiation lies in a region of the spectrum which will affect a photo-cell. The immediate necessity for such measurements lay in the use of the "life-period" method of estimating the speeds of reaction between metal atoms and halogen compounds in the vapour phase.

In this estimation the metal atoms (in a carrier gas) are led through a nozzle into the reaction vessel, where they meet the vapour of the halogen compound in such amount that the whole of the metal atoms react before they can reach the walls of the reaction vessel. By suitable adjustment of the temperature of the reaction vessel and of the rate of entry of metal atoms and halogen compound (the concentration of the latter being kept uniform over the reaction zone), a stationary state of the reaction can be obtained, when the metal atoms form a kind of "flame" above the nozzle. This "flame," which throws a shadow when illuminated by the resonance radiation of the metal in question, is most dense immediately above the nozzle opening, and falls away to zero at the edges. It can be shown ^{1, 2} that if n is the number of metal atoms entering the reaction vessel in unit time, c is the concentration of halogen compound in the reaction zone, and N is the total number of uncombined metal atoms in the reaction vessel (*i.e.*, in the "flame") at a stationary state of the reaction, then the velocity constant k is given by

$$k = \frac{1}{c} \cdot \frac{n}{N},$$

or since $N/n = \tau$ is the average "life-period" of a metal atom in the reaction vessel,

$$k = \frac{1}{\tau c}.$$

The chief experimental difficulty is clearly the measurement of N , since n and c involve only the measurement of temperatures and pressures. In the method as hitherto used, ^{1, 2} the quantity of sodium vapour in the reaction vessel at a stationary state of the particular reaction, has been calculated from photographic measurements of the absorption of sodium resonance light by the mass of sodium vapour. This photographic method is extremely laborious and slow, several days being

¹ Frommer and Polanyi, *Trans. Faraday Soc.*, 1934, **30**, 519.

² Fairbrother and Warhurst, *Trans. Faraday Soc.*, 1935, **31**, 987.

required for the point-by-point photometry of the photographs and the subsequent evaluation from these measurements of the total amount of sodium in a single "flame." It was suggested by Professor Polanyi (*private communication*) that an enormous increase of speed and ease of working could be secured if the mass of metal vapour could be estimated by a few, almost instantaneous, readings of a galvanometer deflection, as could be done if the total absorption could be measured photo-electrically, and the maximum density of sodium atoms in the path of the light were kept within a region where the absorption was a linear function of the concentration. This was the main object of the present work.

There were two main issues in this problem: (a) the experimental problem of the measurement of the absorption; and (b) the investigation of the limits within which the absorption in question is a linear function of the concentration of sodium atoms, *i.e.* the limits within which the manual integration of the sodium atoms can be replaced by an optical one.

As a result of these absorption measurements (which will be discussed later) and from practical considerations of apparatus dimensions and intensity of incident light, it was found necessary to limit the total absorption by a "flame" to about 5 to 10 per cent. of the pencil of light entering the reaction vessel. It should be pointed out that under usual working conditions, the "flame" covers only a part of this pencil of light. The percentage absorption of the whole pencil (which is what is measured) is therefore much less than the average absorption over the cross-section of the flame itself. To use the photo-electric method with the required accuracy, it was therefore necessary to measure the deflection of the galvanometer operated by the photo-cell to within ± 0.1 per cent. It is to be noted that in this work we are not concerned with the measurement of the absolute intensities of the light, but only with the relative changes in the intensity due to absorption by a mass of sodium vapour.

Moreover, as we have shown,² and as is to be expected on theoretical grounds, the absorption factor of the light from the high-frequency metal vapour lamp decreases as the temperature of the lamp is raised to increase the intensity of the emitted light. It was therefore necessary to strike a balance between a falling absorption and a rising intensity of the light. The optimum conditions were given by a temperature at which the lamp gave a light of fairly small intensity. The practical problem, therefore, which was one of some difficulty, was the measurement, with a high degree of precision, of a change in intensity (due to absorption) of a comparatively feeble pencil of light.

The technique of the measurement of light by photo-cells has received much attention in recent years, and the literature on the subject is voluminous. We were, however, unable to find any method described in detail which was well suited to this particular problem. Most of the well-known methods apply to fairly bright sources of light. We considered that the "time of charging of an electrometer" method, as used for feeble illuminations, was not likely to give the required openness of scale, stability of zero and mechanical robustness. We were, therefore, led to develop a combined photo-cell and direct-current amplifier unit, which could be mounted on the reaction apparatus in place of the camera used in the photographic method.

² Fairbrother and Tuck, *Trans. Faraday Soc.*, 1935, 31, 520.

Experimental.

The photo-cell was specially chosen to have a high insulation resistance, high sensitivity in the desired spectral region and a minimum "dark" current. These conditions were satisfied by a G.E.C. cell of vacuum type, with a rubidium oxide-on-silver cathode and with internal and external guard rings. The direct current through this cell when illuminated by the sodium lamp was far too small to be measured directly with the desired accuracy, even by a galvanometer of the highest sensitivity. It was necessary, therefore, to amplify the current passing through the cell, and the construction of a sufficiently sensitive, yet stable and robust direct current amplifier, was one of the major difficulties in this work.

A number of designs of balanced D.C. amplifiers using electrometer tetrode valves have appeared in the last few years. These have chiefly related to the expensive American F.P.54 valve: a review of the different circuits used has been given by Penick.⁴ We have found, however, that an entirely satisfactory balanced amplifier can be constructed by using the T113 electrometer tetrode valve of the German Osram Konzern.* The only previous publication describing the use of this valve in such a circuit appears to be that of Barth,⁵ who used a slightly different circuit from the present one.

Since such a D.C. amplifier, or balanced valve electrometer, has many uses beyond the present one, and since suitable values for the various resistances for use with this valve (the choice of which involves some labour), do not appear to have been published, the method of balancing and the resistances actually used in the present work are given in some detail.

The starting-point in this work was a circuit described by DuBridge and Hart Brown.⁶ This was subsequently modified in order to render it more flexible and more suitable for use with the T113 valve. The final circuit, arrived at independently, was essentially the same as the one described by Harnwell and van Voorhis,⁷ and used by them with the F.P.54 valve and a valve developed by the Bell Telephone Laboratories, and known as Type D-96475 Electrometer Tube.

The circuit diagram and values of resistances used in the present work are shown in Fig. 1. Since the mathematical theory of similar circuits has been described previously,^{6, 7} it will not be repeated here: but it may be stated that the practical aim in selecting the resistance values is to secure that the galvanometer deflection passes through a rather flat minimum when the filament current is varied over a small range through the rated value. Harnwell and van Voorhis arrived at suitable resistance values for use with their valves, by carefully measuring the various tube derivatives and solving the appropriate equations. The rather more empirical method described below was used in the present case, and was found to be quite satisfactory.

The T113 valve has a thoriated filament, rated by the makers to take 100 m.a. at 3 volts, a space charge or inner grid round the filament, and a very highly insulated control grid between the space charge grid and the anode. After some preliminary experiments with the valve, it was decided to use the rather high control grid bias of -4.5 volts, i.e. the control grid being at least 7.5 volts negative to the more positive end of the filament. The maximum safe anode voltage was deemed to be 9 volts to minimise the production of positive ions in the residual gas. The high control grid bias was chosen in order to stabilise the control grid current: the immediate result of such a bias, however, with the anode and the inner grid

⁴ Penick, *Rev. Sci. Instr.*, 1935, 6, 115.

* We are indebted to Dr. J. C. Brentano for bringing this valve to our notice.

⁵ Barth, *Z. Physik.*, 1934, 87, 399.

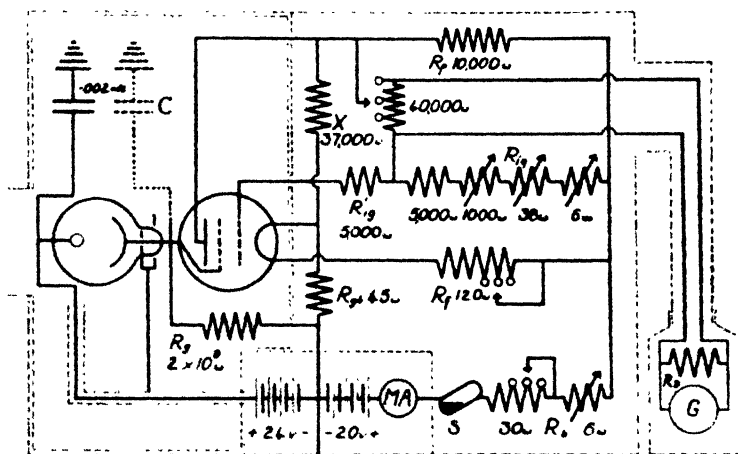
⁶ DuBridge and Hart Brown, *Rev. Sci. Instr.*, 1933, 4, 532.

⁷ Harnwell and van Voorhis, *ibid.*, 1934, 5, 244.

at the same potential (~ 9 volts) was that the anode current was very small, most of the current being taken by the inner grid. The potential of the latter was therefore reduced to about 4.5 volts, by the inclusion of the 5000 ohm resistance R'_{lg} in the bridge network.

The bridge network was then set up as shown in Fig. 1 (with the exclusion at first of the resistance X). The anode resistance R_p was made approximately of the same value as the dynamic resistance of the plate-filament circuit, in order to give an approximately equal ratio arm bridge. Under these conditions the four resistances of (a) the plate-filament circuit; (b) the inner grid-filament circuit, together with R'_{lg} ; (c) R_p ; and (d) R_{lg} comprise the four arms of a resistance bridge, across two corners of which the galvanometer (with its Ayrton shunt and critical damping resistance R_D) is placed, and which is capable of being brought to balance in the usual way by the adjustment of R_{lg} .

The effect of varying the filament current by adjustment of R_b , or by a change in the E.M.F. of the battery during use, is in the first place to alter the relative values of (a) and (b), and to a smaller extent the voltage applied to the corners of the bridge. The procedure adopted, therefore,



PHOTOMETER CIRCUIT

FIG. 1.

was to balance the bridge by means of R_{lg} (i.e., bring the galvanometer deflection approximately to zero), for various values of the filament current, as shown by the meter M.A., in an endeavour to find values of the variable resistances, such that the galvanometer deflection passed through a flat minimum on variation of the filament current alone. With the values of R_p , R'_{lg} , and R_{lg} given in Fig. 1, variations in which are limited by the operating conditions of the valve, it was found (and will, in general, be found for similar valves) that this stabilisation occurred at a filament current which was far removed from the rated value. This difficulty could be overcome most conveniently by the inclusion of a large resistance X shunted across the plate circuit. Various fixed resistances were tried in this position, the effect of several of which is shown in Fig. 2, in which galvanometer deflection is plotted against filament current. The required resistance clearly lies between 35,000 and 40,000 ohms. A resistance of 37,000 ohms was therefore constructed and resulted in stabilisation at about 99 m.a. filament current, which is close to the rated value, and at which the filament was run thereafter. The inclusion of this resistance X reduces slightly the sensitivity of the bridge, but the present form of the latter was found to be very sensitive, and ample for the purpose

required. The voltage sensitivity, using a Moll galvanometer of 6×10^{-9} amp./mm. was 9600 mm./volt: this corresponds to a sensitivity of 115,200 mm./volt with a galvanometer of a sensitivity of 5×10^{-10} amp./mm., as used by Harnwell and van Voorhis with an F.P. 54 valve, and is therefore about 5 per cent. greater than they obtained.

The fixed resistances used in the bridge circuit, and those with tapplings, were made of Manganin wire wound on slotted ebonite strips. The variable resistances were of conventional type as used in radio work, with the exception of the 6-ohm fine adjustment resistances in R_{lg} and R_b :

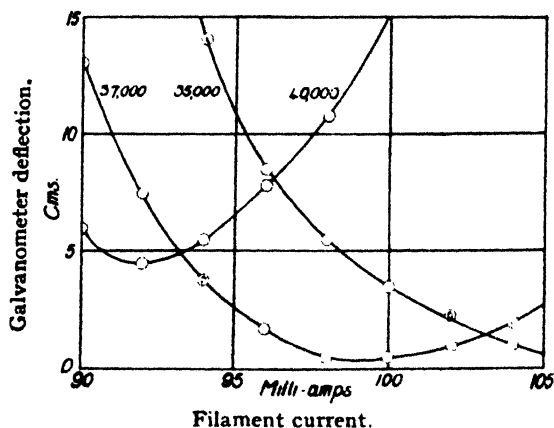


FIG. 2.

for these, no suitable commercial type could be found which would give a sufficiently fine and smooth variation. They were therefore made in the form of spiral slide-wires, about 100 cms. in length, wound on coarse, ebonite spirals of 9 turns.

An important feature of the apparatus was the inclusion of an air-dielectric condenser C , of $0.002 \mu F$ capacity and high insulation resistance, between the grid of the amplifier valve and earth. This

condenser, together with the grid resistor, increased the time-constant of the circuit to about 2 seconds, and therefore gave a corresponding time-average of the response of the photo-cell. This was a necessary provision in order to allow for fluctuations in a reaction "flame" when this is used as an absorbing medium. Moreover, the inclusion of this condenser rendered the circuit very insensitive to stray high-frequency fields: probably much of the final success of the apparatus, which is used within a few feet of a powerful short-wave oscillator, is due to this condenser, and to the electrical screening which is described later.

High Resistances.

In order to amplify the current through the photo-cell, it must pass also through a high resistance R_g , the voltage drop across which is applied to the grid and filament of the amplifier valve. The construction of a suitable resistance for this purpose was almost an investigation in itself. We were unable to buy suitable commercial resistances, and after many trials, in which were tried various compositions, and also evaporated and sputtered films of platinum and gold, on glass rods, a successful resistance was finally prepared by evaporating gold on to Pyrex glass rods which were kept at a temperature of $300^\circ C$. Earlier experiments with sputtered and evaporated metallic films resulted in resistances which were satisfactory for a time, but whose value gradually increased on standing. This was attributed to slow changes in the structure of the film, and therefore the metal was condensed on to the support at a sufficiently high temperature to permit of the formation of a stable structure.

The method of preparation was as follows. Two 10 cm. lengths of 0.1 mm. diam. tungsten wire were twisted together with a gold wire of similar diameter. This composite wire was then wrapped with very thin tungsten wire in the form of an open spiral, and the complete assembly arranged so that it could be heated electrically in a horizontal vacuum tube. After the wire had been given a preliminary heating in vacuo to remove grease

and tungstic oxide several carefully cleaned Pyrex glass rods (about 10 cm. \times 0.3 cm.), the ends of which had been previously platinised with "liquid platinum" (as used in ceramic work), were arranged in the vacuum tube, parallel to the wire. The vacuum tube was then surrounded by an electric furnace at about 300° C., and outgassed before the evaporation of the metal. The latter was carried out simply by passing a current through the composite gold-tungsten wire: the gold, on melting, ran into the spaces between the tungsten wires which formed a carrier, so that little was wasted, and the metal could be raised well above its melting-point. The same technique was used for the evaporation of platinum. After cooling, the gold-covered rods were removed and their resistances measured. As the metal film was thickest on one side, that nearest the evaporator wire, and tapered off at the edges, the resistance could easily be adjusted by scraping to fall within a desired range. After the resistance had been so adjusted, wires were tightly twisted round the platinised ends and the whole rod immersed in melted Piccin to give protection from the atmosphere, since it was found that the films gradually deteriorated on exposure to the air.

The photo-cell, electrometer valve, grid resistance and condenser, were mounted inside a vacuum-tight, earthed copper tube, with walls $\frac{1}{4}$ -inch thick. The photo-cell was fixed with its cathode opposite a plate glass window in the side of the tube, and was screened inside the tube from stray light from the valve filament. The copper tube was evacuated to a pressure less than 1 mm. Hg, thus avoiding trouble with electrical leaks due to ionisation of the air or to deposition of atmospheric moisture or other impurities on the parts of the very sensitive grid circuit. The rest of the amplifier, including the batteries, was housed in an earthed copper box, and was switched on by the mercury contact switch S, to avoid variable switch-contact resistance. The high-frequency oscillator and the metal vapour lamp were also screened as far as practicable by enclosure in a tinned iron box with metal gauze panels for ventilation.

Using the photo-cell described above, and a grid resistance of 2×10^9 ohms, which gave about twice the required light sensitivity, the galvanometer deflection became steady in about fifteen minutes after switching on, and thereafter there was no detectable drift of the light-spot over a period of many hours. The amplitude of the instability variations was less than 1 mm. (in 1000 mm. deflection) and averaged about 0.5 mm. These residual fluctuations are probably due to the Flicker effect of the cathode of the electrometer valve. The complete apparatus was therefore suitable for the measurement of a change in the intensity of the beam of light, with a precision of ± 0.1 per cent. of the intensity of the unabsorbed beam. The linearity of the galvanometer deflection/light intensity relation was tested by a movable light source and the application of the inverse square law, and also by an addition method using two light sources. The curve departs from linearity only to the extent of 1 or 2 per cent. Some idea of the sensitivity of the photometer may be gained from the fact that a moderately glowing cigarette end, at a distance of several feet from the photo-cell, will produce a galvanometer deflection of more than 1000 mm.

Such a stable and sensitive photometer demanded naturally an equally stable light source. The high-frequency sodium vapour lamp responds instantly to even small changes in the voltage of the anode supply to the oscillator, and at first minute variations in the commercial A.C. supply could be followed by movements of the galvanometer light spot. As it was impracticable to use accumulators for the anode battery of the oscillator, as was done for the filament battery, a rectifier and smoothing unit was constructed to give 1000 volts: this was then reduced to the 500 volts necessary for the oscillator by a series resistance and four Cossor S. 130 neon tubes arranged in series and placed in parallel across the output. This arrangement completely smoothed out any fluctuations due to variations of the A.C. mains.

The high-frequency lamp was enclosed in a large thermostatically controlled air-oven, constant to $\pm 0.05^\circ\text{C}$. The lamp, however, is sensitive to temperature changes of far less than this, and with such a degree of thermostatic control, the photometer galvanometer light-spot was still subject to a very regular periodic excursion of about $\pm 12.5\text{ mm}$. about a mean position of $\sim 1000\text{ mm}$. deflection. The period of this variation corresponded exactly to the operation of the thermostatic cut-off, and was due to temperature changes in the lamp, caused by the heating and cooling of the oven. Since a thermostatic control sufficiently fine to eliminate this variation was impracticable, the following device was adopted. A simple beam-splitting device was constructed by arranging a plane mirror at an angle of 45° to the beam from the lamp, a portion of the silvering in the centre of the mirror being removed. The direct beam through the hole in the silvering, passed to the photo-cell, whilst the major portion of the light was reflected on to the surface of a Weston Photronic cell. The current

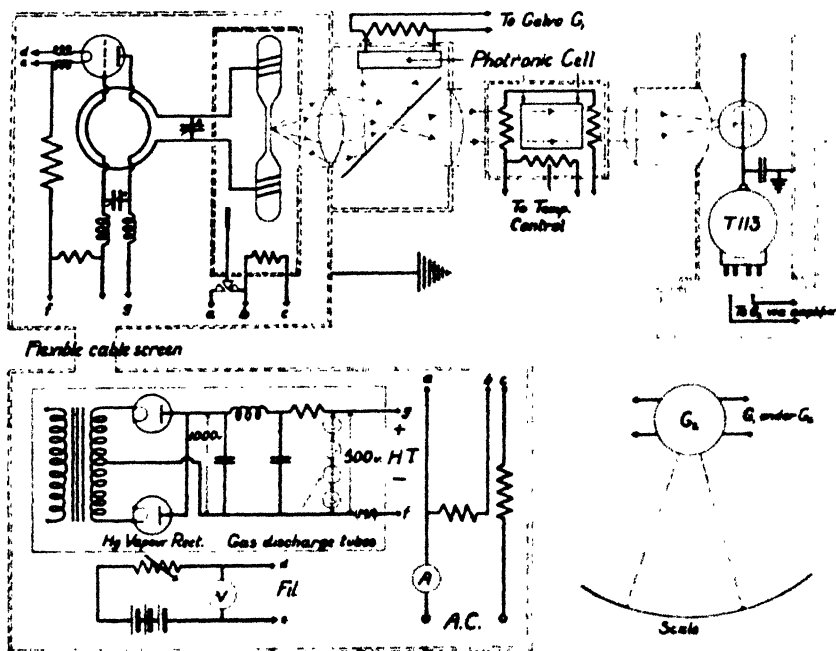


FIG. 3.

from the latter was measured by a second Moll galvanometer (high current sensitivity type), whose light-spot moved over the same scale as that of the photometer galvanometer. By suitable adjustment of the sensitivity of this second galvanometer, small variations in the intensity of the light source were made to produce the same amount of movement of the two galvanometer light-spots. Changes in the intensity of the main beam passing into the photometer were then made by observing the differences between the two galvanometer deflections. Since, under these conditions, the Photronic cell was operating at an almost constant illumination, non-linearity of the relation between the light flux and the current output of the cell did not affect the result. Moreover, in the final arrangement of the apparatus as required for reaction velocity measurements, the photometer must be at some distance from the light source and the beam of light nearly parallel, and therefore the utilisable area of the light source must be small, much smaller, in fact, than the actual flat emitting surface of the lamp. In this beam-splitting device an image of the emitting surface

of the sodium lamp is formed by a large aperture lens on the mirror, the hole in which then acts as a stop, and defines the new source, the light from which is then made parallel by another lens, and the major portion of the light from the lamp is reflected on to the Photronic cell. Thus, by the use of light which would otherwise be wasted, we are able to use the less sensitive Photronic cell as a zero device. The optical arrangement and general disposition of the apparatus is shown in Fig. 3.

The results of a number of absorption measurements are given in Figs. 4 and 5. In these measurements the direct beam through the hole in the mirror silvering passed through a cell filled with sodium vapour and contained in an air oven, and into a condensing lens in front of the

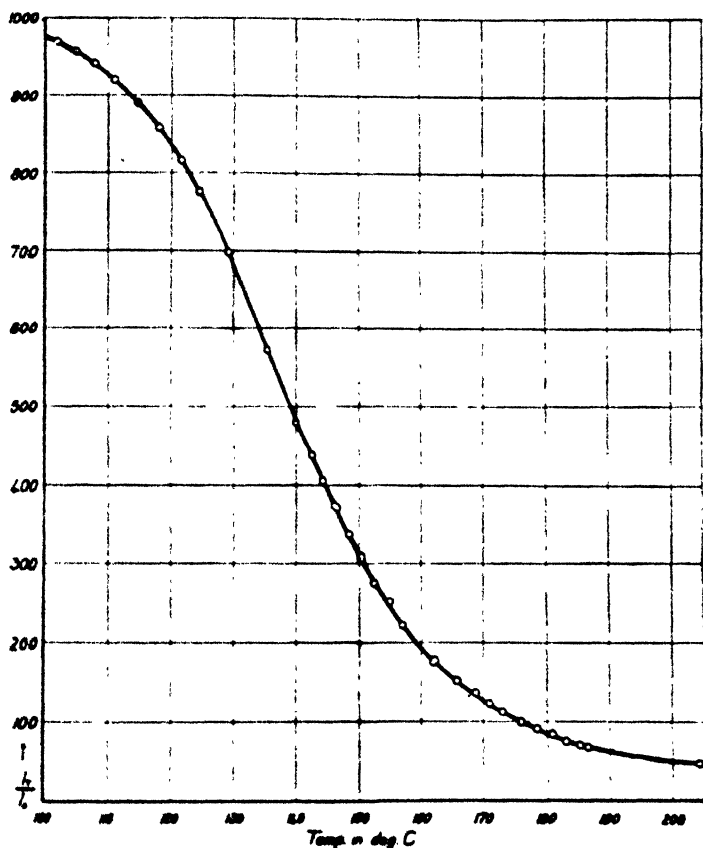


FIG. 4.

photo-cell. The sodium cell was made of Jena glass, about 3 cm. diameter, with plane ends 4.64 cm. apart, and contained a small quantity of sodium, distilled into it in vacuo. The high-frequency lamp was operated at a temperature of 210° C., and the absorption was followed almost down to the melting-point of sodium. In Fig. 4, I_t/I_0 (intensity of transmitted light/intensity of incident light) is given as a function of the absorption cell temperature (the quantity actually measured), and in Fig. 5 (curve A) as a function of the number of moles of sodium per square cm. in the path of the light. The latter has been calculated from the temperature of the absorption cell and the data of Ladenburg and Thiele.⁸ Since, however,

⁸ Ladenburg and Thiele, *Z. physik. Chem.*, 1930, **7B**, 161.

the lowest temperature investigated by these authors was 180°C ., the vapour pressures at lower temperatures were obtained by plotting their results in the form of $\log . p$ against $1/T$ and extrapolating: there must still exist therefore the slight uncertainty of this extrapolation.

In Fig. 5 also (curve B), $\log . I_t/I_0$ is plotted as a function of the number of moles of sodium per square cm. in the path of the light obtained in the same way.

These absorption measurements were made in several stages, between which major adjustments to the apparatus were made, such as re-heating of the absorption cell and re-charging of the batteries in the amplifier: the various portions of the curve "fit" perfectly, and repeat measurements made common regions showed a reproducibility within ± 0.1 per cent.*

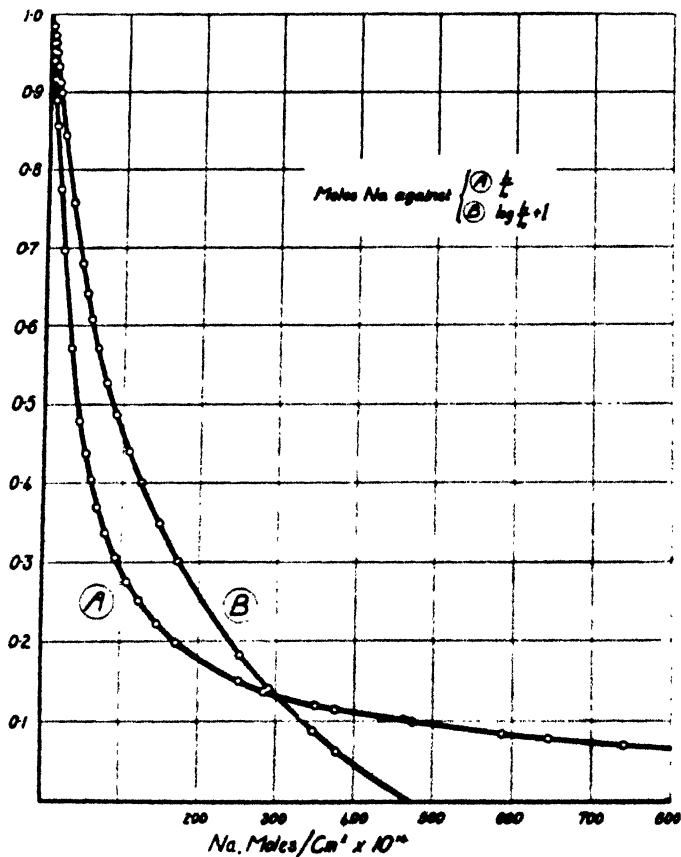


FIG. 5.

When light is absorbed by a homogeneous coloured solution, the absorption $\log . I_t/I_0$ is a linear function of the concentration of the absorbing material (Beer's law). We cannot, however, deduce the concentration in a system of variable absorbing density, from the *total* absorption, by this exponential relation. We therefore, as mentioned earlier in the paper, required to know the range of sodium density over which I_t/I_0 was a linear function of the number of sodium atoms in the path of the light. When the results shown in Fig. 5 are plotted on a larger scale, they show that I_t/I_0 is a linear function of the amount of sodium concerned, up to about

* We should like to thank Mr. E. Warhurst for much assistance with these absorption measurements.

45 per cent. absorption, whilst Beer's law is followed only up to about 25 per cent. absorption.

We may therefore take a mass of sodium vapour of variable density, the maximum absorption by any part of which is, say, x per cent. of the light incident on that part, and calculate the total number of sodium atoms in the system on the assumption that the absorption of any region is a linear function of the mean absorption and the number of sodium atoms in that region. Our aim in the beginning was to make this maximum absorption x equal to 25 per cent. to 30 per cent. of the light, with a total absorption of 10 per cent. (These figures were arrived at from an examination of records of "flames" obtained by the photographic method.) As can be seen from curve A, however, this can be extended to nearly 45 per cent. maximum absorption.

Summary.

1. A sensitive photo-electric photometer has been developed for the measurement of the intensity of a beam of sodium resonance light, with a precision of ± 0.1 per cent.
2. For this purpose a stable, balanced D.C. amplifier (which may also be used as a valve electrometer) has been constructed, using an Osram T113 electrometer valve.
3. The technique of making electrical resistances of very high value, by evaporating gold on to glass rods, is briefly described.
4. Some photo-electric measurements of the absorption of sodium resonance light are given, extending down almost to the melting-point of sodium.
5. It is found that I_t/I_0 (intensity of transmitted light/intensity of incident light) approximates very closely to a linear function of the number of sodium atoms in the path of the light, up to about 45 per cent. absorption of the light.
6. It is also found that Beer's law is obeyed in this absorption, over a much smaller range.

In conclusion we wish to thank Prof. M. Polanyi for his advice and help throughout this work, and Messrs. Imperial Chemical Industries, Ltd., and the Department of Scientific and Industrial Research, for research grants.

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REACTIONS BETWEEN SODIUM VAPOUR AND VOLATILE POLYHALIDES. VELOCITIES AND LUMINESCENCES.¹

BY W. HELLER AND M. POLANYI.

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The diffusion method devised by H. von Hartel and M. Polanyi* (see Fig. 1) was applied to the reactions of sodium vapour with the following substances:

BCl_3 , BBr_3 , CCl_4 , SiCl_4 , SiBr_4 , GeCl_4 , SnCl_4 , TiCl_4 ,
 PCl_5 , AsCl_3 , SbCl_3 , S_2Cl_2 , COCl_2 , POCl_3 , CrO_2Cl_2 , CS_2 .

¹ An extract of this paper was given in *Compt. rend.* 1934, 199, 1118.

² *Z. physikal. Chem.* 1930, 11B, 97.

The list contains nearly all the completely chlorinated or brominated polyhalides which have a sufficient vapour pressure to be introduced at room temperature into the "diffusion apparatus." The present study is in the nature of a general survey in which the emphasis is on the determination of the sequence of reactivities and on the observation of a series of chemiluminescences which made their appearance while the reaction velocities were measured.

Experimental Procedure.

Preliminary to the study of these reactions, one of the authors (W. H.), in conjunction with Dr. Kodama and Mme. Schatunowskaja, has made an extensive re-examination of the diffusion method which is to be submitted shortly to this journal.

The following were the main results of this investigation. The distribution of the halogen compound throughout the flame region in the stationary state was determined for various velocities (v) of the "carrier gas," using different carrier gases (N_2 , H_2) at different pressures, resulting in different values for the diffusion constant (δ) of the sodium vapour in the carrier

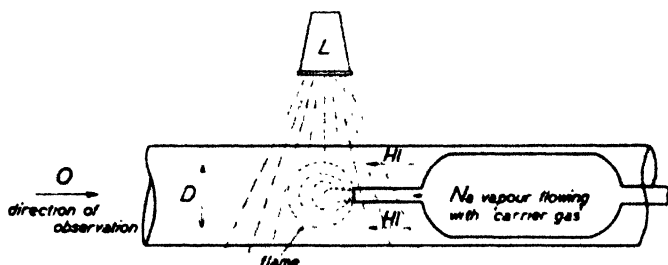


FIG. 1.—Main Features of the "Diffusion Method."—Na-vapour is carried by a flow of carrier gas into the reaction vessel, where it meets the flow of a gaseous halogen compound HI ("halogen gas"). The reaction zone is illuminated by a sodium resonance lamp (L), the sphere of sodium vapour thus made luminescent is the "flame," the diameter D of which is measured. D is estimated through a window at O by a sighting device which is adjusted successively to the upper and to the lower edge of the "flame."

gas. It was established that conditions must be so adjusted that v/δ (v in m./sec. and δ in cm.²/sec.) should be between 5×10^{-3} and 12×10^{-3} , since at higher values the halogen compound is "swept out" of the flame region, while at lower values the back diffusion into the nozzle falsifies the results. The conclusion was also reached that the measurement should be based on flames of large size, if possible not smaller than 3.5 cm. in diameter.

Various improvements relating to the control of the inflowing "halogen gas" stream lead to a more accurate determination of the partial pressure of the halogen gas in the reaction zone. At the same time, a more reliable estimation of the flame diameter was introduced by "end on" observation with a levelling device adjustable to the edges of the flame. The method thus improved, yields relative velocity constants of about 15 per cent. accuracy for reactions requiring not less than about 50 and not more than about 5000 collisions.

Apart from these technical developments, of which full use has been made in the present work, special provisions were made for the handling of the halogen compounds, most of which are extremely sensitive to moisture, and attack tap-grease and mercury. The purchased halogen compounds were opened in vacuo and distilled into the apparatus. The flow of halogen

gas was controlled by valves of the membrane type (Fig. 2) and the mercury in the manometers covered with sulphuric acid or paraffin oil. Owing to these technical difficulties the capillaries, by which the flow of the halogen gas is controlled, could be calibrated only for a few of the inorganic polyhalides. The flow of the other halogen gases was calculated on the assumption that the viscosity of the vapours does not differ appreciably. This was found to be true in a comparison carried out between CCl_4 and SiCl_4 as well as between a large number of halogenated organic compounds. It is believed that the error caused by the assumption of equal viscosities cannot affect the sequence of reactivities as stated below.³

The reaction rates of CCl_4 , SiCl_4 , BCl_3 , BBr_3 , TiCl_4 fall within the range stated previously for which we estimate the accuracy of the relative values to be about 15 per cent. The other compounds react so fast as to lie beyond the range of velocities for which the method can be used quantitatively; in these cases only the order of magnitude of the reaction rates could be established. As to the sequence of values given for this group of substances, we see no reason why the sequence of any pair of values differing by more than 30 per cent. should not be correct.

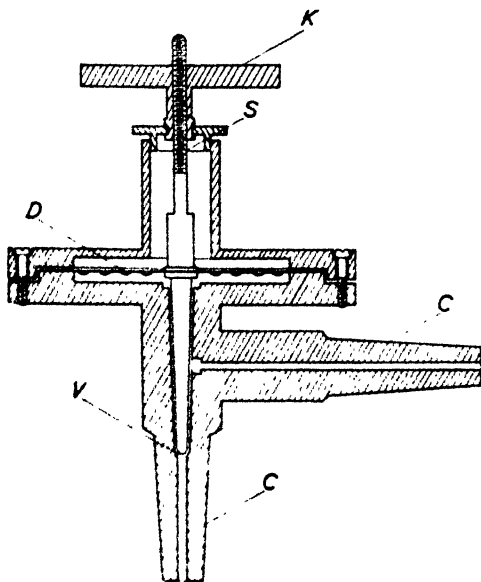


FIG. 2.—Rotation of the knob K moves the screw S vertically. This motion is transmitted through the metal vacuum-tight diaphragm D to the needle, which can thus be raised or lowered into the valve seating V. The cones C are used to connect the valve to the apparatus.

Reaction Velocities.

The results listed in Table I. all refer to a reaction temperature of 270° . The partial pressure p_{Na} of sodium at the nozzle was nearly $3 \cdot 10^{-3}$ mm.; deviations from this value were duly taken into account. The carrier gases used were H_2 and N_2 (the former for faster, the latter for slower reactions), and their pressures were varied from 1 mm. to 10 mm. Each reaction velocity was determined by a series of measurements on flames of different sizes; on the average five flames were measured, ranging in size from 2 cm. to 4.5 cm. The values listed in the table are interpolated for the size of 3.5 cm.

The calculation of the velocity constants is based on the formula

$$k = \frac{\left(\ln \frac{p_{\text{Na}}}{p_0} - \ln \frac{R}{r} \right)^2}{(K - r)^2} \cdot \frac{\delta}{p_{\text{H}_2}} \cdot \frac{1}{T^2}$$

³ For a determination of the absolute values of reaction rates the distribution of the halogen gas throughout the flame has to be taken into account. The influence of this correction will be shown in the detailed communication on the improvements of the experimental method, where specific reference will once more be made to the case of CCl_4 .

TABLE I.

Compound.	Reaction Velocity Constant k (c.c. mole ⁻¹ sec. ⁻¹ $\times 10^{-11}$).	Collision Number (S).
BCl ₃	4.71	1,350
CCl ₄	963	6.5
SiCl ₄	4.03	1,570
TiCl ₄	993	6.4
GeCl ₄	4,890	1.3
SnCl ₄	3,510	1.8
PCl ₃	1,500	4.2
AsCl ₃	1,470	4.3
SCl ₂	6,340	1.0
BCl ₃	4.71	1,350
BBr ₃	248	25.6
SiCl ₄	4.03	1,570
SiBr ₄	1,450	4.4
S ₂ Cl ₂	1,760	3.6
SCl ₂	6,340	1.0
PCl ₃	1,500	4.2
POCl ₃	2,290	2.8
COCl ₂	856	7.4
CrO ₂ Cl ₂	1,330	4.8
CS ₂	~ 0.306	207,500

where p_N and p_0 are the partial pressures of sodium at the centre and at the edge of the flame respectively, p_0 being 10^{-6} mm.; R and r are the radii of the flame and the nozzle respectively, r being 0.25 cm.; δ is the diffusion constant of sodium vapour in the carrier gas, and was calculated for the prevailing conditions on the basis of earlier determinations⁴ by which the values $\delta_{H_2} = 3.14$ and $\delta_{N_2} = 0.92$ had been obtained for atmospheric pressure, and 643°K .; p_H is the partial pressure of the halogen gas in the reaction chamber and T the absolute temperature. The reaction velocity constants k are in the units of c.c./mol. sec.

The "collision numbers" (S) also listed in the table are based on a uniform collision diameter of $6.7 \cdot 10^{-8}$ cm. We thus obtain the relation

$$S = \frac{6.3 \times 10^{14}}{k}.$$

The molecular velocities of the halogen compounds range between 17,000 and 34,000, which are the values for COCl_2 and SiBr_4 respectively. This causes a variation in the collision no. of ± 3 per cent. which has been taken into account in the evaluation of S .

In the table we have grouped our results in the following way. The chlorides are listed in the sequence of their position in the periodic system of elements. Then the bromides (BBr_3 and SiBr_4) are shown in juxtaposition to the corresponding chlorides. The next section points out the effect of a change in valency of the atom to which the halogen is linked; finally, the values for COCl_2 , CrO_2Cl_2 and CS_2 are given.

We note in the first part of the table that there is a considerable inertia attached to the reactions of BCl_3 and SiCl_4 ; the inertias of CCl_4 , TiCl_4 , PCl_3 and AsCl_3 are noticeable; the reactions of GeCl_4 , SnCl_4 and

⁴ H. von Hartel, N. Meer and M. Polanyi, *Z. physik. Chem.* 1932, 19B, 139.

SCl_2 are practically instantaneous. If we add to the data listed in the first section of the table, the fact that the reactions of sodium vapour with Cl_2 , Br_2 and I_2 are all instantaneous, we cannot fail to observe that the tendency for an inertia to be present falls off when we pass from the third and fourth groups to the higher groups of the system. The fact that the volatile halogenides of the second period (HgCl_2 , CdCl_2 , ZnCl_2 , CuCl_2) all react instantaneously suggests that the inertia has its maximum in the middle groups of the periodic system, and falls off both towards lower and higher groups. This corresponds to the changes in bond strength of the halogen atoms which are highest for the middle groups of the periodic system.

The second part of the table illustrates the increase in reactivity caused by substituting Br for Cl; a rule repeatedly observed previously in the organic series. The ratio of the velocities of the Cl and Br-compounds is similar to that found in the organic series.

An increase in reactivity, corresponding to decreasing bond strength, is also found in the two cases where compounds corresponding to a higher valency stage can be compared with compounds of a lower valency stage: SCl_2 reacts faster than S_2Cl_2 ; POCl_3 faster than PCl_3 . (The oxygen atom introduced in the latter case seems to have little effect, since COCl_2 does not react faster than CCl_4 .)

A measure of bond strength most appropriate to our problem is given by the restoring forces of the bonds, as derived from Raman spectra. Table II. illustrates the parallelism of the "inertia" deter-

TABLE II.

Compound:	Collision Number (S).	Restoring Force Constants ($f \times 10^{-4}$) between Central Atom-HI-Atom.
CCl_4	0.5	2.00
SiCl_4	1.570	2.42
TiCl_4	0.4	2.20
GeCl_4	1.3	—
SnCl_4	1.8	2.00
PCl_3	4.2	1.9
AsCl_3	4.3	1.4
SbCl_3	—	0.87
BiCl_3	—	0.44
CH_3Cl	7,100*	3.12
CH_3Cl_2	310*	2.94
CHCl_3	22*	2.47
CCl_4	2*	2.00
CH_3Cl	7,100*	3.12
CH_3Br	75*	2.61
CH_3I	1	2.15

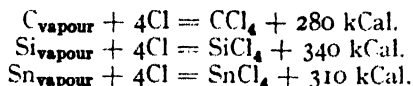
* These values which have been substituted for the earlier results of Hartel, Meer and Polanyi are based on new measurements of W. Heller to be published shortly.

mined by the collision number, with the restoring force constant f of the bond. Within each of the three groups, $\text{CCl}_4 \rightarrow \text{SnCl}_4$, $\text{CH}_3\text{Cl} \rightarrow \text{CCl}_4$ and $\text{CH}_3\text{Cl} \rightarrow \text{CH}_3\text{I}$ this parallelism holds equally well.

The high restoring force attributed to the linkages in SiCl_4 might appear unexpected; ^a it is, therefore, to be noted that it is borne out by

^a K. W. F. Kohlrausch, *Der Smekal-Raman Effekt*, 1931, page 217, expresses diffidence as to the correctness of this force constant for this reason.

the heat of formation of SiCl_4 which is considerably higher than that of either CCl_4 or SnCl_4 . We have the energies



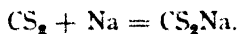
It seems reasonable that the force which counteracts an elongation of the halogen bond should also be responsible for the chemical inertia of such reactions which lead to the splitting up of the bond. A closer consideration of the theoretical connection of force constant and chemical inertia has been given by R. A. Ogg in conjunction with one of the authors.⁶

Reaction of CS_2 with Na-Vapour.

We found that Na-vapour reacts with CS_2 -vapour. In view of the endothermicity of the process,



the observed reaction appears to be the addition

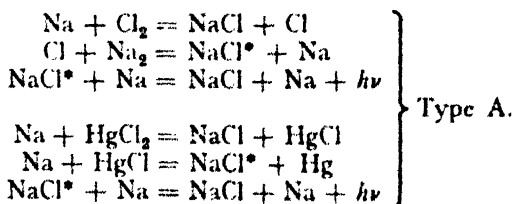


The fact that the reaction proceeds very slowly helps to confirm this view. The observed velocity constant k (Table I.) which was measured in the presence of 6 mm. of pentane used as carrier gas, is not too large to be accounted for by three-body collisions. Indeed, the reaction is slower than in the case of the analogous reaction between Na-vapour and O_2 to which reference is made later.

Chemiluminescences.

The chemiluminescence accompanying the reaction of sodium vapour with chlorine was discovered by Haber and Zisch.⁷ When a nitrogen stream at atmospheric pressure, carrying a slight admixture of sodium vapour, was led into chlorine a slight yellow glow appeared which was found to contain exclusively the D-line of sodium.

By the use of "highly attenuated flames" this luminescence was greatly increased in intensity, and the mechanism of its origin was elucidated.⁸ At the same time, a number of similar luminescences were discovered, accompanying the reactions of Na-vapour with the various halogens and with the volatile halogen salts of the second sub-group of the periodic system. Two examples may show the mechanism of these luminescences



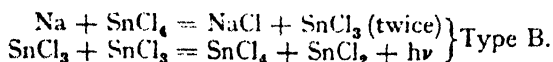
⁶ *Trans. Faraday Soc.*, 1935, **31**, 482.

⁷ *Z. Physik*, 1922, **9**, 302.

⁸ H. Beutler and M. Polanyi, *Z. physik. Chem.*, 1928, **113**, 3.

In both cases the final process of excitation consists in a collision of the "nascent" NaCl^{*}-molecule with an Na-atom. Such chemiluminescences can arise only if there is a reaction of Na-vapour which evolves at least 48.5 kCal. which is the molar excitation energy of the D-line.

A chemiluminescence differing fundamentally from these was observed⁹ when highly attenuated sodium vapour was brought into reaction with SnCl₄-vapour. The luminescence has a continuous spectrum, the origin of which is supposed to be



Since, according to this view, the luminescence arises from two particles as they undergo the process of reaction, this type (B) has been given the name of "primary chemiluminescence." The atomic mechanism which may lead to primary chemiluminescence was discussed in detail in a recent paper by R. A. Ogg and one of the authors.¹⁰ An obvious condition for the occurrence of this sort of luminescence is the presence of a heat of reaction (*E*) satisfying the condition

$$E \geq Nh\nu_1$$

where ν_1 is the short-wave limit of the continuous spectrum emitted by the reaction.

A third type (C) of chemiluminescence, the mechanism of which is still unexplained, was discovered when CuCl₂ vapour was brought into a flame of Na + Cl₂. Besides the yellow light belonging to the Na + Cl₂ flame, an intense green luminescence made its appearance in which the well-known CuCl-bands were recognised spectroscopically. The same luminescence also arises when CuCl₂ is brought into an Na + HgCl₂-flame, and it was observed also when CuCl₂ was introduced into a stream of atomic hydrogen reacting with chlorine; it is distinctly observable in the gas phase when chlorine attacks metallic aluminium in the presence of CuCl₂ vapour.¹¹ The peculiar feature of these latter luminescences lies in the fact that although no emission of light accompanies the reaction between CuCl₂ with either Na-vapour or H-atoms or metallic aluminium, the presence of another body, such as Cl₂ or HgCl₂ reacting simultaneously with these substances gives rise to the luminescence.

The chemiluminescences newly observed in connection with the reactions of the inorganic polyhalides seem to belong partly to type A or B; another group which made its appearance only when O₂ was added to the flame, shows some similarity to type C, but may prove to represent an altogether new type.

Table III. presents the observations on chemiluminescence. With (CCl₄, SiCl₄, AsCl₃ and CS₂, no luminescence was observed; accompanying the reaction of TiCl₄ there sometimes appeared a faint glow, but the existence of this luminescence could not be definitely established. Clearly visible luminescences were present in the reactions of BCl₃, BBr₃, SiBr₄, GeCl₄, SnCl₄ (as previously known), PCl₃, S₂Cl₂, SCl₂, COCl₂, POCl₃ and CrO₂Cl₂ with sodium vapour.

⁹ M. Polanyi and G. Schay, *Z. Physik*, 1928, 47, 814.

¹⁰ R. A. Ogg and M. Polanyi, *Trans. Faraday Soc.*, 1935, 31, 1375.

¹¹ L. Frommer and M. Polanyi, *Z. physik. Chem.*, 1930, 6B, 371. This paper gives only a brief account of other CuCl-luminescences than those caused by the reaction with aluminium. Details of the other cases have remained unpublished.

TABLE III.

Halogen Compound.	Observed Luminescence, Colour.	Estimated Intensity (I _{SnCl₄} = 10).	Probable Luminescence Type.
BCl ₃	grey	1-2	B
CCl ₄	—	0	—
SiCl ₄	—	0	—
TiCl ₄	blue*	< 1	—
GeCl ₄	blue	10	B
SnCl ₄	blue	10	B
PCl ₃	D-line	2-3	A
AsCl ₃	—	0	—
SCl ₂	bluish (continuum extending from yellow to violet)	10	B
BCl ₃	grey	1-2	B
BBr ₃	blue	3-5	B
SiCl ₄	—	0	—
SiBr ₄	yellow	5-7	B
S ₂ Cl ₂	blue	2-4	B
SCl ₂	bluish	10	B
PCl ₃	D-line	2-3	A
POCl ₃	bluish-grey	7-9	B
COCl ₂	D-line	9-10	A
CrO ₂ Cl ₂	bluish-greenish-grey	10-15	B
S ₂ Cl ₂	blue	2-4	B
S ₂ Cl ₂ + O ₂	D-line	> 10	C
SCl ₂	bluish	10	B
SCl ₂ + O ₂	D-line	> 10	C
S ₂ C	—	0	—
S ₂ C + O ₂	D-line	> 10	C
POCl ₃	bluish-grey	7-9	B
POCl ₃ + O ₂	bluish-grey	7-9	B
CrO ₂ Cl ₂	bluish-greenish-grey	10-15	B
CrO ₂ Cl ₂ + O ₂	bluish-greenish-grey	10-15	B

* Existence doubtful.

The luminescences of the reactions of COCl₂ and PCl₃ with Na-vapour consist of the D-line; these cases, therefore, probably belong to type A. For COCl₂ the reaction might be

- (a) $\text{Na} + \text{COCl}_2 = \text{NaCl} + \text{COCl}$,
 (b) $\text{Na} + \text{COCl} = \text{NaCl}^* + \text{CO}$,
 (c) $\text{NaCl}^* + \text{Na} = \text{NaCl} + \text{Na} + h\nu$.

The heat of formation of COCl₂ from CO and 2Cl-atoms being 82 kCal., and the formation heat of two NaCl (vapour) from the atoms being 190 kCal., either reaction (a) or (b), and possibly even both, might possess a reaction heat of more than 48.5 kCal., which are necessary for the excitation of Na vapour. It seems probable, however, that such a reaction

heat is present only in reaction (b). No detailed suggestion can be given for the mechanism of the PCl_3 luminescence.

The luminescence of GeCl_4 is in every respect similar to that of SnCl_4 , and might be accordingly accounted for by a mechanism of type B. Of the other chlorine compounds, only SbCl_3 has a considerable intensity of chemiluminescence. Its spectral character appears to be a continuous band, extending from yellow to violet; very similar to the spectrum of the SnCl_4 and GeCl_4 luminescences. On this evidence it might be classified with these in group B. The luminescences of S_2Cl_2 and BCl_3 appear to be of similar character, but the light was too faint to permit a clear determination of the spectral character.

It is interesting to note that the reaction of SiBr_4 is luminescent, although that of SiCl_4 is not. There is a similar relation between BBr_3 and BCl_3 ; the luminescence of the bromine compound is considerably more intense than that of the chlorine compound. The rather incomplete spectral evidence indicates that the luminescence of SiBr_4 and BBr_3 belong to type B.

A very intense luminescence is obtained with CrO_2Cl_2 , and a somewhat less bright one with POCl_3 . Both luminescences are not of the colour of the D-line, and in consequence cannot belong to type A, but are probably of the type B.

There is a marked connection between the occurrence of the luminescences which we have classed under the type B, and the velocity of the reaction from which they arise. Of nine substances yielding a luminescence of this type, eight react instantaneously with sodium vapour. BCl_3 , which forms an exception to this rule, gives only a very faint luminescence.

Not only do all luminescences emitting other light than that of the D-line (with one exception) come from instantaneous reactions, but also conversely, all the instantaneous reactions of polyhalides hitherto observed are accompanied by such luminescences.

A further series of luminescences appeared when oxygen was added to the reaction mixtures of CS_2 , S_2Cl_2 and SbCl_3 (Table III.). Sodium vapour and oxygen react with one another according to Haber and Sachsse,¹² through the primary formation of NaO_2 , which is subsequently stabilized by collisions with the carrier gas; this reaction is accompanied by no visible luminescence. The reaction between sodium vapour and CS_2 is, as was pointed out above, probably of a similar type to that of $\text{Na} + \text{O}_2$, and it likewise shows no trace of luminescence; it is only the mixture of O_2 , CS_2 and Na which emits light. It is a bright radiation of the colour of the D-line.

The two luminescent reactions of sodium vapour with S_2Cl_2 and SbCl_3 are also profoundly modified by the addition of oxygen; a strong emission of the D-line arises in the presence of which the original luminescence can no more be observed; it could not be established whether it had actually vanished, or had only become invisible when outshone by light which arises on the addition of oxygen. Oxygen had no effect on the luminescences of POCl_3 and CrO_2Cl_2 .

The luminescences caused by the addition of oxygen resemble the luminescences classed above, under type C, which also require the presence of three reacting substances. We can offer no suggestion for this mechanism, and can note only that sulphur is present in each of the observed cases.

¹² *Z. physik. Chem., Bodenstein Festband*. 1931, 831.

Size of the Luminescent Zone.

The luminescent zone is of the same shape as the area filled with sodium vapour, by which the reaction zone (or "flame") is usually characterised (see Fig. 1). In the cases listed in Table IV. we have

TABLE IV.

Halogen Compound.	Diameter <i>D</i> of the Resonance Flame.	Diameter <i>D'</i> of the Luminescence Flame.	<i>D/D'</i> .
SnCl ₄	1.235	1.03	1.20
"	1.365	1.02	1.34
"	2.41	1.76	1.37
"	2.95	1.765	1.67
"	3.45	2.145	1.61
"	4.14	2.695	1.54
GeCl ₄	1.72	1.54	1.12
PCl ₃	2.99	~ 1.5	~ 2.0
"	3.66	~ 2.0	~ 1.8
"	3.99	~ 2.0	~ 2.0

measured the diameters both of the luminescent zone and of the sodium "flame"; the former appears to be always smaller than the latter. This proves that the light is stronger in the central parts of the "flame"; a fact easily to be explained by relating the intensity of the luminescence to reacting quantities per time and volume unit, which are higher in the interior parts of the flame than at its periphery.

Summary.

1. The reaction velocities of a series of polyhalides (BCl₃, BBr₃, CCl₄, SiCl₄, SiBr₄, GeCl₄, SnCl₄, TiCl₄, PCl₃, AsCl₃, SCl₂, S₂Cl₂, COCl₂, POCl₃, CrO₂Cl₂) reacting with sodium vapour have been determined by use of the "diffusion method."
2. Owing to the extreme rapidity of most of the reactions the rates of a few only could be quantitatively determined, while the order of magnitude and the sequence of reactivity were established for the rest. The polyhalides of the elements belonging to the middle groups of the periodic table show the highest inertia in reacting with Na-vapour.
3. In a homologous series the chemical inertia increases with the restoring force acting in the halogen linkage.
4. Na-vapour reacts with CS₂-vapour; probably by a three-body collision.
5. Thirteen different new luminescences were observed arising from the reactions of Na-vapour with BCl₃, BBr₃, SiBr₄, GeCl₄, PCl₃, SCl₂, S₂Cl₂, COCl₂, POCl₃, CrO₂Cl₂, and from a mixture of Na-vapour and O₂ reacting with CS₂, SCl₂, and S₂Cl₂. A classification of these chemiluminescences according to principles previously established has been attempted.

The above experiments were carried out in the Kaiser Wilhelm Institut für Physikalische Chemie from January to August, 1933. The authors wish to recall in deep gratitude the memory of F. Haber who, during this period, was Director of the Institute.

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THE ABSORPTION OF GASES ON SODIUM CHLORIDE.

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Comparatively few adsorption measurements have been obtained with gases, at low pressures, on crystal surfaces. Langmuir¹ has shown that the adsorption of a number of gases on mica at 90° K., 155° K., and 183° K. can be represented by his theoretical equation. Bawn² has confirmed this with carbon monoxide and oxygen, but he could find no simple relation to express the results obtained with argon. He assumed that this gas covered more than one elementary surface, and that the equation must therefore be written:—

$$x = \frac{\sum K_1 c_1 c'_1 p}{1 + \sum c'_1 p},$$

where K_1 , K_2 , etc., denote the relative areas of the various surfaces. The magnitude of these constants will largely determine the shape of the isotherm. Both he and Langmuir calculated that the thickness of the adsorbed layer was never greater than monomolecular, although the percentage of the surface covered at saturation varied considerably with different gases. The surface of mica is a complex distribution of atoms, and Langmuir suggests that the unsaturated carbon monoxide is adsorbed on all types of surfaces, whereas oxygen, for example, is only attached to the metallic atoms, and hence will have a low saturation value.

Durau³ has studied the adsorption of various gases on sodium chloride at higher pressures, and optical examinations of the adsorbed layer of methanol on a single crystal of this salt have been made by Silvermann⁴ and Frazer.⁵ They find the layer to be monomolecular, but Whipp;⁶ however, in an attempt to explain the abnormal form of the isotherm in the adsorption of iodine by crystals of potassium chloride, has postulated the formation of a second layer at higher pressures.

There are, unfortunately, few data available to verify the calculations of Lennard-Jones⁷ concerning the nature and magnitude of the adsorptive forces operative at the surface of crystals. A preliminary survey of the adsorption of ten gases by sodium chloride crystals at 90° K. and 183° K., at low pressures has therefore been made in order (a) to test the possibility of lateral diffusion of adsorbed molecules; (b) to measure their heats of adsorption at low temperatures; and (c) to correlate the adsorbability of the gases with their physical properties.

¹ Langmuir, *J.A.C.S.*, 1918, **40**, 1361.

² Bawn, *ibid.*, 1932, **54**, 72.

³ Durau, *Ann. Physik.*, 1928, **87**, 307.

⁴ Silvermann, *Physic. Rev.*, 1930, **36**, 311.

⁵ Frazer, *ibid.*, 1929, **34**, 97.

⁶ Whipp, *Proc. Roy. Soc.*, 1933, **141A**, 217.

⁷ Lennard-Jones, *Trans. Faraday Soc.*, 1928, **24**, 92.

Experimental.

Preparation of Materials.

Sodium Chloride.—Very small and fairly uniform crystals were obtained by passing a rapid stream of pure hydrochloric acid gas into a saturated solution of A.R. sodium chloride. After two precipitations, the salt was filtered through a ground glass plate, and dried in a vacuum dessicator over caustic potash and phosphorus pentoxide, for a month. The average dimensions of the crystals (assumed to be cubic) were measured by a high-power microscope. The mass of the salt was 65.4 grams, and its total surface area was estimated to be approximately 45,000 sq. cms.

Argon.—Impure argon and oxygen were sparked between platinum electrodes for six hours. Oxides of nitrogen were absorbed by 40 per cent. caustic potash and excess oxygen was removed by combining with freshly reduced copper at 350° C., and the argon finally dried over phosphorus pentoxide.

Carbon Monoxide.—100 per cent. formic acid was added to concentrated sulphuric acid, and the gas purified by passing over caustic potash and through a liquid-air trap, and dried by phosphorus pentoxide.

Methane was prepared for this work by Dr. M. W. Travers from dilute hydrochloric acid and aluminium carbide and purified by repeated fractional distillations.

Oxygen.—Pure potassium permanganate was heated and the gas passed over solid caustic potash and phosphorus pentoxide.

Nitrogen.—This gas was supplied by Dr. Travers, and was obtained from ammonia, which had been purified by fractional distillation, by oxidation, using a mixture of copper oxide and copper at 400° C. The latter prevents the formation of any oxides of nitrogen. Water vapour was removed by condensation in a liquid-air trap.

Nitric Oxide.—50 per cent. sulphuric acid was added to a mixture of two parts by weight of potassium nitrate, and one part of potassium iodide.⁸ The gas was passed over caustic potash and phosphorus pentoxide and condensed into a liquid-air trap. The nitric oxide was kept in the liquid state while a further supply of the gas was passed through it, in order to remove any nitrous oxide present.⁹ The product was then repeatedly distilled and fractionated. The last traces of nitrogen and nitrous oxide were removed by twice subliming the nitric oxide under a pressure of 17 mm., and finally condensing it at 50 mm. pressure. Analysis was performed by mixing with pure oxygen and absorbing the nitrogen peroxide by monoethylamine.¹⁰

Nitrous Oxide.—Cooled concentrated hydroxylamine hydrochloride was added to sodium nitrite solution. The gas was passed through caustic potash solution, and concentrated sulphuric, and dried over phosphorus pentoxide. The product was fractionated repeatedly, and its purity tested by measuring its vapour pressure at -78.2° C.

Carbon Dioxide.—This was obtained from sodium bicarbonate and dried over phosphorus pentoxide.

Cyanogen.—Pure mercuric cyanide was heated and the cyanogen condensed and fractionated.

Ethylene.—A mixture of concentrated sulphuric acid and ethyl alcohol was heated to 160° C. The gas was passed through caustic potash solution cooled in a freezing mixture and then fractionated.

Apparatus.

The apparatus, which is shown diagrammatically in Fig. 1, consisted of a calibrated gas burette, C, two McLeod gauges, M₁ and M₂, together

⁸ Winkler, *Ber.*, 1901, 34, 1408.

⁹ Gray, *J.C.S.*, 1905, 87, 1601.

¹⁰ Koehler and Marqueryrol, *Bull. Soc.*, 1913, 13, 69.

with the system A, and a duplicate blank one, B. These latter contained adsorption vessels, V_1 and V_2 , liquid-air traps, T_1 and T_2 , and mercury seals, bd and cg , and were such that their total volume and total glass surface were the same. Pointers, a, b, c, d, e and f , etc., were fused into the seals in order that the mercury levels could be adjusted to definite positions. The volumes of the traps and the vessels were determined before being incorporated in the apparatus. All glass tubing was of 1 cm. internal diameter. The apparatus could be exhausted by a glass-mercury diffusion pump, backed by a Hyvac oil pump, to a pressure of less than 1×10^{-6} cm. mercury. The two gauges had a range from 1×10^{-4} to 1×10^{-1} cm., and were accurately calibrated. The gas burette was used in the determination of the volumes of the various systems and also for the admission of gas during adsorption measurements.

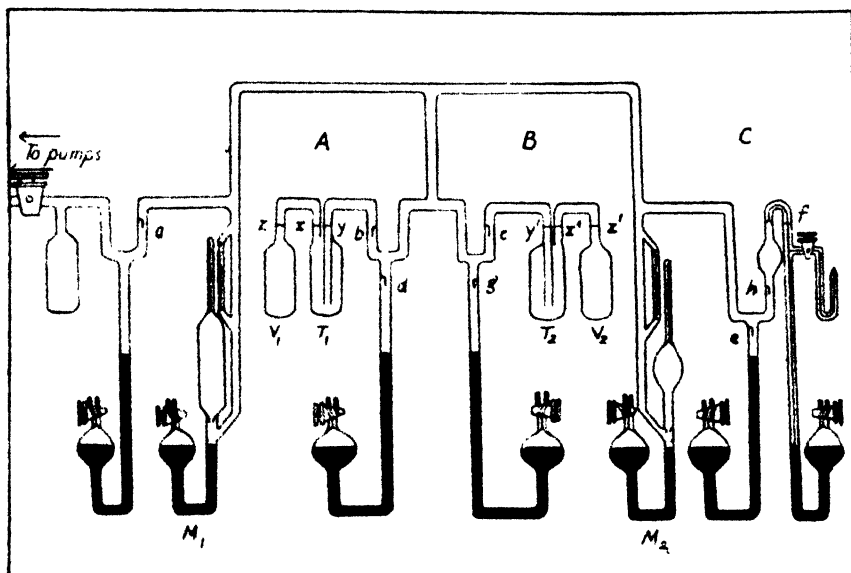


FIG. 1

Calibrations.

Hydrogen was used throughout, since it is not appreciably adsorbed on glass at 90°K . (¹ and ²). A known quantity was admitted into the various systems from the gas burette, and the volumes calculated by means of the gas laws. Extensive calibrations were made in order to correct for the thermomolecular flow which occurs at temperature junctions at low pressures. These are recorded elsewhere.¹¹

Procedure.

Outgassing of the surface was effected by evacuating the adsorbent at 350°C ., for sixteen hours, during which time the trap T_1 was immersed in a bath of solid carbon dioxide and alcohol for the first fourteen hours, and in liquid air for the remaining two. The salt was cooled for two hours, after which period a small pressure of hydrogen was admitted and the adsorption vessel immersed in liquid air for an hour. The hydrogen was then pumped out. This procedure accelerated the establishment of thermal equilibrium, since otherwise the chief mode of heat distribution in a hard vacuum is by conduction through the adsorbent itself, which has a low

¹¹ Tompkins and Wheeler, *Trans. Faraday Soc.*, 1933, **29**, 1248.

thermal conductivity. The cooling process had no effect on the magnitude of the adsorption, but without it, spurious rate curves had been obtained with the first admission of the adsorbate.

During adsorption measurements, the system B, was cut off by the U-seal, *cg*, and after outgassing and cooling, the pumps and the vessel, V_1 , were isolated by the seals, *a* and *b*. Gas was admitted from the gas burette and the seals levelled to *e* and *f*. From the pressure recorded in the McLeod gauge, the amount introduced was calculated. This was expanded into the system, A, and the equilibrium pressure recorded. This is not the pressure in the gauge, since corrections have to be applied for thermo-molecular flow. From the calibration curves,¹¹ the actual pressure in the vessel, V_1 , can be easily found. The amount of gas remaining in the gas phase—again with the appropriate corrections—was thus known, and the difference of this and the quantity initially introduced, measured the adsorption on the salt and on the glass. The adsorbent was again isolated,

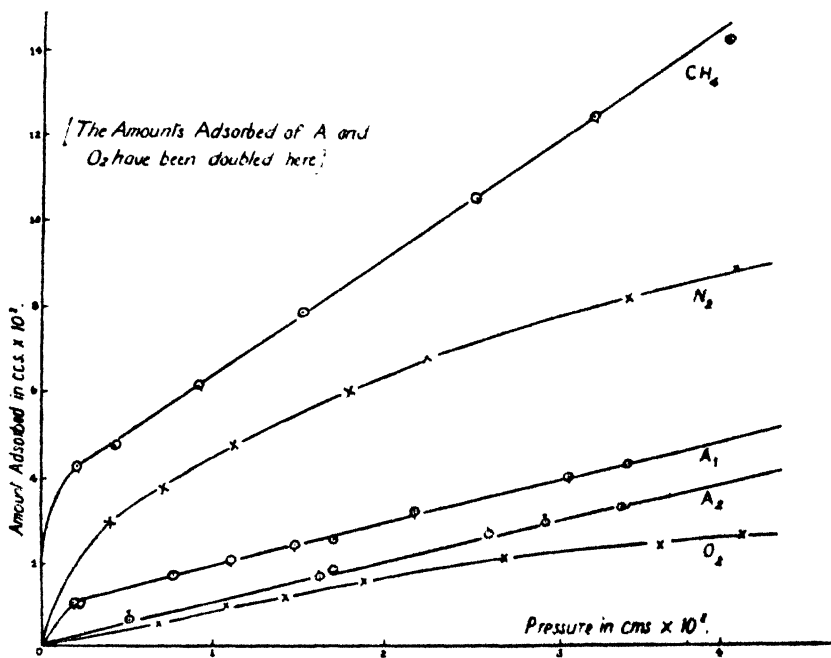


FIG. 2.

the pressure measured, and a further amount of gas introduced. The increase of pressure gave the magnitude of the additional quantity, and hence the total amount of gas admitted. This was expanded into the system, A, and the amount adsorbed at this higher equilibrium pressure calculated as before. The process was repeated until a pressure of 4×10^{-3} cm. was reached. The series was then discontinued, since the accuracy decreases with each addition of gas. The amount adsorbed, however, at any pressure was quite independent of the number of increments by which the pressure was built up. Similar measurements in the system, B, were made under identical conditions, in order to measure the adsorption on the glass surface alone. This was so small that it has been neglected.

Results.

Adsorption of Argon.

The amount of argon adsorbed at any pressure at -183°C. depends largely upon the conditions of outgassing. Typical isotherms (Fig. 2,

A_1 and A_2) show that there is a large, but variable adsorption at low pressures, but that Henry's law is obeyed at higher concentrations, and that the plots are parallel to one another. It is suggested that the first few milli-c.c. are adsorbed on high potential areas of the surface such as, at re-entrant angles, or linearly along the mouths of Smekal cracks. Outgassing, therefore, affects the potential and extent of such areas, but the main surface is unaltered.

After a carbon monoxide isotherm had been determined, the adsorption of argon was reversible and reproducible, but the amounts were smaller in magnitude than in any previous determination. The strongly unsaturated carbon monoxide, which covers nearly all the surface, had probably partially poisoned the active centres, and outgassing at 350°C . was ineffective in removing it. Even when the temperature was raised to 500°C ., the initial portion of the argon isotherm was practically unchanged, thus showing that these active areas had not been affected. The car-

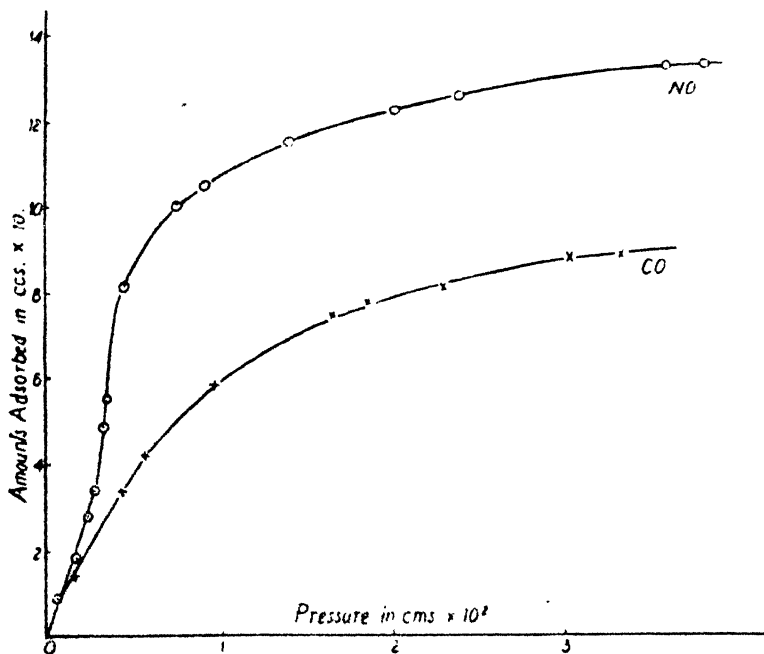


FIG. 3.

bon monoxide isotherm, however, was lowered. Sintering had probably occurred, causing the coalescence of micro-crystals on the main surface, thus reducing the effective area of the adsorbent. Argon isotherms determined subsequent to this, were also lower than those previously obtained. This was probably due to an increase in the poisoning action of carbon monoxide. Methane isotherms also showed a decrease, similar to that of carbon monoxide. The adsorbent was then treated with oxygen at 500°C . in order to remove the carbon monoxide chemically as carbon dioxide, but this caused a further decrease in the adsorption of argon. Treatment with hydrogen and also with carbon monoxide at 350°C ., had no effect. Chemisorption, or surface chemical reaction with the formation of a small amount of sodium oxide¹³ had probably occurred, since the introduction of hydrochloric acid gas restored the surface to its original condition after a further outgassing. Although the surface was probably

¹³ Lange and Dürr, *Z. Elektrochemie*, 1926, 32, 85.

slightly contaminated with carbon monoxide, no further attempts were made to clean it. Argon isotherms, which were periodically determined, showed however that it possessed constant adsorptive capacity and remained in a steady condition throughout all subsequent measurements.

Adsorption of Argon, Methane, Oxygen, Nitrogen, etc.

Isotherms obtained with these gases on the above surface at -183°C . are collected together in Figs. 2 and 3. The adsorption of all of them at -78.2°C . was too small to be measured. Fig. 4 gives isotherms obtained with cyanogen, nitrous oxide, carbon dioxide and ethylene at this latter temperature and on the same surface.

A few measurements with argon, methane and carbon monoxide were made at -192°C . (liquid nitrogen), in order to obtain values for the heat

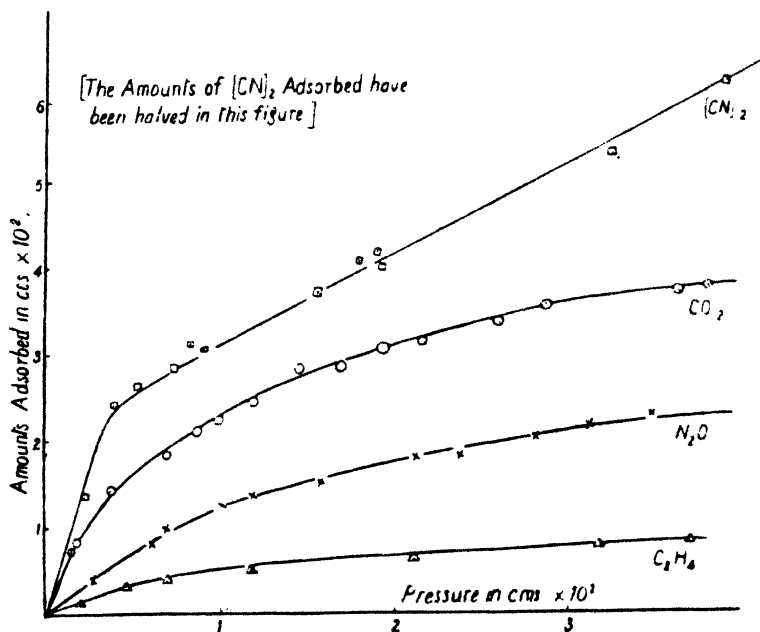


FIG. 4.

of adsorption, by comparing the amounts adsorbed at -192°C ., and at -183°C . The argon isotherm at -192°C . differed from that at the higher temperature only in the magnitude of the initial process, and the plots were parallel at higher pressures. Consequently, there is no change in the amount adsorbed with temperature in this region and the calculated heat of adsorption is zero. A value of 300 Cals. was obtained with methane at higher concentrations. Bawn (*loc. cit.*) gives 334 Cals. for the heat of adsorption of this gas on mica at low temperatures. In the present investigation a heat of 350 Cals. was found for carbon monoxide, and this remained constant throughout the pressure range studied. In his theoretical calculations, Lennard-Jones¹³ has given 3000 Cals. as the heat of adsorption of argon on sodium chloride, but with the later data of London,¹⁴ this has been reduced¹⁵ to 1000-1500 Cals. Wilkins¹⁶ finds that the

¹³ London, *Z. physik. Chem.*, 1931, 11 B, 222.

¹⁴ Lennard-Jones, *Trans. Faraday Soc.*, 1932, 28, 333.

¹⁵ Wilkins, *ibid.*, 1932, 28, 438.

latter figure is in better agreement with his experimental results. Lenel,¹⁶ however, supports the former, both theoretically and experimentally. He has, however, assumed that the Langmuir equation is applicable, and, moreover, no correction was made for thermo-molecular flow and the adsorption was measured at low concentrations, where higher values are to be expected, since high potential areas are covered initially.

It is perhaps a coincidence, rather than significant, that the same type of isotherm is obtained with gases which are isosteres. The isotherms of carbon monoxide and nitrogen, and of carbon dioxide and nitrous oxide follow the Langmuir equation closely; those of oxygen and ethylene obey the Freundlich expression, and those of argon and methane show similar characteristics.

Discussion.

A quantitative treatment of the adsorptive forces, which are operative at the surface of heteropolar crystals, has been given by Lennard-Jones.¹⁴ They comprise (a) van der Waals, or dispersive forces, which according to London,¹³ are approximately proportional to the square root of the van der Waals constant, a , and which represent general forces of adhesion, analogous to gravitation; (b) electrostatic forces, which become important when the adsorbent is a metal, or is composed of ions and the adsorbate is polar; (c) polarisation forces, which are produced by the surface field inducing a non-uniform charge distribution in the adsorbed molecule; and lastly, (d) a much smaller force, which has not, as yet, been evaluated and which represents the reaction of the adsorbent to the charges on its surface. It is shown by London (*loc. cit.*) that the adsorption on amorphous substances is largely controlled by the van der Waals forces, but the electrostatic forces are the more important in the adsorption of gases on metals (Lennard-Jones¹⁴). The calculations of Lennard-Jones emphasise the small contribution of the electrostatic forces in the adsorption on crystal surfaces, and therefore the adsorbability of gases on sodium chloride should follow the magnitude of their respective van der Waals a constants, and thus be comparable to that on homopolar adsorbents.

Table I. gives the adsorption of nitric oxide, carbon monoxide, methane, nitrogen, argon and oxygen at -183°C. , and of cyanogen, carbon, dioxide, nitrous oxide and ethylene at -78.2°C. , in c.c. at 0°C. and 760 mm. pressure, at pressures of 1 and 2×10^{-2} cm. mercury, together with the comparative data of Bawn and Langmuir for the adsorption of gases on mica at -183°C. These latter figures represent the percentage saturation, *i.e.* the percentage of the surface covered at saturation. The amounts of methane, carbon monoxide and of argon adsorbed on the glass in the present series at -183°C. , at 1×10^{-2} cm. pressure are also given. The remaining columns give the values of the polarisability of the gases, according to London,¹³ the van der Waals a constant, and the electric moment of the dipole molecules in the appropriate units.

With all gases, the amounts adsorbed are small and since there is always a rapid attainment of equilibrium, the process entirely reversible, and the heats of adsorption are low, the adsorption must be van der Waals in character. There is however no simple relationship between the van der Waals constant and the adsorbability, such as that indicated by London and suggested by the calculations of Lennard-Jones. Attention is drawn to the extremely large adsorption of the two polar gases,

¹⁶ Lenel, *Z. physik. Chem.*, 1933, **23 B**, 379.

TABLE I.

Gas.	T° C.	Adsorption in c.c. N.T.P.			% Saturation.		$\alpha \times 10^{24}$.	$a \times 10^6$.	$\mu \times 10^{18}$.
		On Salt.		On Glass.	Mica.				
		Press.		Press.	Bawn.	Lang- muir.			
		0'01 cm.	0'02 cm.	0'01 cm.					
NO	-183° C.	1'07	1'22	—	—	—	—	267	0'16
CO	-183° C.	0'594	0'810	0'0006	1'13	0'38	—	296	0'10
CH ₄	-183° C.	0'064	0'089	0'0059	—	0'68	2'58	449	0'00
N ₂	-183° C.	0'040	0'062	—	—	0'22	1'74	277	0'00
A	-183° C.	0'0055	0'0100	0'0003	0'30	0'17	1'57	268	0'00
O ₂	-183° C.	0'0041	0'0082	—	0'23	0'11	1'63	276	0'00
(CN) ₂	-78'2° C.	0'065	0'0832	—	—	—	—	1528	0'30
CO ₂	-78'2° C.	0'0230	0'0330	—	—	—	—	716	0'00
N ₂ O	-78'2° C.	0'0121	0'0174	—	—	—	—	754	0'17
C ₂ H ₄	-78'2° C.	0'0043	0'0070	—	—	—	—	889	0'00

nitric oxide and carbon monoxide, at -183°C. , although the value of their α constants are smaller than that of methane, which is not strongly adsorbed. This peculiarity seems to be confined to heteropolar surfaces, since the results of Bawn on mica, and of Durau³ on sodium chloride at 0°C. , show that carbon monoxide is more highly adsorbed than methane, whereas the reverse is found on glass, and on charcoal.¹⁷ It must, therefore, be concluded that it is the electrical forces occurring at the heteropolar surface, together with the dipole character of the adsorbate, which largely decides the amount of gas adsorbed. The dipole moment is again the important factor in the adsorption of gases at -78.2°C. , with the exception of carbon dioxide which is discussed later. Cyanogen, for example, has the largest moment, and is most highly adsorbed, whereas the adsorption of the non-polar, unsaturated ethylene is exceedingly small. The dipoles carried by polar molecules, however, will contribute only in a minor degree to the value of the van der Waals constant, owing to the random movement of the molecules in the gas phase. Since the magnitude of this constant determines the adsorbability of a gas on a homopolar adsorbent, the possession of a dipole moment will cause little increase in the amount of gas adsorbed. With a heteropolar surface, dipoles are attached to it in an oriented manner, and thus considerably increase the electrostatic force, and so cause a large increase in the adsorption.

Nevertheless, the theoretical curves giving the variation of van der Waals and electrostatic forces as functions of the distance of the adsorbed molecule from the surface of a crystal,⁷ show that the contribution of the latter to the total adsorption potential, at the normal equilibrium distance of 3 to 4 Å., is much less than that of the van der Waals forces. The electrical forces are short ranged in effect, but, since they increase with extreme rapidity, they become the larger at smaller distances. The great effect produced by the presence of small dipoles on the adsorbability of the gases on sodium chloride, suggests that a closer approach

¹⁷ Arrhenius, *Medd. Nobelinst.*, 1911, 2, 7. (As to adsorption on glass, see Table I, above.)

of the molecules to the surface occurs. This is possible from spatial considerations, but it would necessitate a large increase in the heat of adsorption, unless there was a correspondingly large increase in the electrostatic repulsive forces. Herzfeld¹⁸ has shown that these would contribute a large negative part to the total heat and would also fix the equilibrium position. They are certainly important in the adsorption of gases on metals, and in such systems the electrostatic forces do account for the greater part of the adsorption potential, as, for example, in the adsorption of nitrogen on copper.¹⁴ A metal, however, is a perfectly polarisable system; nevertheless, there must be a similarity in the surface fields of metals and ionic crystals, since a metal is built up of a lattice of positive ions with free electrons approximately uniformly distributed between them. This similarity is emphasised in the above results, where it is seen that the electrostatic forces control to a large degree the magnitude of the adsorption. It must, therefore, be concluded that, either the approach of the adsorbed molecule to the surface is closer than has hitherto been assumed and that there are large electrostatic repulsive forces operating, or, that a crystal acts as a pseudo-polarisable system, and that the method of electrical images is applicable in the estimation of the electrical forces to the adsorption potential. This latter assumption has been used in a general manner by Magnus in his electrical theory of adsorption.¹⁹

In the adsorption of non-polar gases, the polarisability of the adsorbate is the most important property, as has been deduced by London in his dispersion theory.¹² Methane (Table I.) is the most highly adsorbed, and is the most easily polarisable, whereas oxygen and argon with low polarisabilities are adsorbed approximately to the same small extent. No simple quantitative relation of adsorbability and polarisability is expected, since the equilibrium distances of the adsorbed molecule vary with the gases, and also because the forces operating are not simply due to a mutual polarisation of like molecules, but to forces acting between molecules of the adsorbate and two systems of oppositely charged ions on the surface.

The adsorption of the non-polar carbon dioxide is "abnormal" in so far as the amount adsorbed is larger than that expected from its polarisability. It is probable that this molecule, being linear in structure, becomes attached by the oxygen atoms at two points when adsorbed, and lies flat on the surface. The surface field of the crystal induces an electric charge in one of these, and this is transmitted through the molecule with the result that a charge of opposite sign is produced in the other oxygen atom. Since the distance between the sodium and chlorine ions in the crystal lattice approximates to that between these two atoms, each of these latter will be in the vicinity of an ion carrying a charge, which is opposite in sign to that of the neighbouring oxygen atom. The forces which are holding the molecule to the surface will therefore be considerably increased, and the rate of evaporation retarded. This phenomenon should occur whenever the distance between two like atoms of a linear non-polar adsorbate molecule is about the same as that between two different ions of a crystal surface lattice. Nitrous oxide, on the contrary, is polar, and the molecule does not lie flat on the surface, since oriented adsorption occurs.

¹⁸ Herzfeld, *J.A.C.S.*, 1929, 51, 2608.

¹⁹ Magnus, *Trans. Faraday Soc.*, 1932, 28, 386, etc.

The sharp initial rise in the argon and methane isotherms has been identified with adsorption on active centres. Since the calculated heats of adsorption in the higher pressure range are either low, or zero, it is probable that all of the adsorption occurs on active patches and the straight part of the isotherm at higher pressures merely represents the complete saturation of such patches. The initial adsorption has associated with it a heat of adsorption, since the amount adsorbed in this region varies with the temperature; the linear adsorption, however, does not change with the temperature with argon, and only slightly with methane, as is expected if the additional gas only saturates these active areas. The adsorption of these gases will take place in the neighbourhood of the smaller sodium ion, where the external field is a maximum. Consequently, repulsive forces will act between similar dipoles which are induced in adjacent adsorbed molecules, and these forces will mainly determine the shape of the isotherm. Fuchs²⁰ has shown that isotherms of the same type as found in this work with argon and methane are obtained when such repulsive forces are assumed in a hypothetical one-dimensional adsorption. The presence of small high potential areas is expected to have little effect on the carbon monoxide isotherm, since most of the adsorption is on the main crystal surface, which must be approximately equipotential. This is confirmed by the constant heat of adsorption and the applicability of the Langmuir equation throughout the range of measurements.

The shape of the nitric oxide isotherm indicates the presence of large attractive forces between adsorbed molecules,²⁰ and is comparable to that found by Polanyi and Welke²¹ with sulphur dioxide on charcoal. Nitric oxide covers about 90 per cent. of the measured surface at saturation so that the adsorption must occur over both ions of the crystals. Consequently, induced dipoles of opposite sign are adjacent on the surface and this orientation produces a large attraction between the adsorbed molecules, which will be further increased, particularly at low temperatures, by the presence of the strong electric field at the surface. Since there is evidence, for example, from specific heat²² and vapour pressure measurement,²³ and from the high Trouton constant and the abnormal density at the boiling-point,²³ of the association of nitric oxide in the liquid and gas phase at low temperatures, and since the attraction is much larger when the gas is adsorbed, molecular aggregates are probably formed in the surface layer. At low pressures, Henry's Law is obeyed (Fig. 3). This linear portion represents the adsorption of simple NO molecules, but in the region where the curve rises abruptly, association begins, and as the curve bends over in the normal manner towards saturation, only doublet molecules are adsorbed. It is seen, for example, that the Henry region ends when 0.35 c.c. of gas has been adsorbed, and that the bending over commences when twice this amount has been taken up by the adsorbent.

The adsorption of all gases at -192°C. and -183°C. was almost instantaneous, but at -78.2°C. , a very slow secondary process was found with the highly adsorbed gases. The critical temperature of lateral diffusion must therefore be within these two limits. This is in accord with the value (150°K.) found theoretically by Lennard-Jones.¹⁴

²⁰ Fuchs, *Z. physik. Chem.*, 1933, **21B**, 235.

²¹ Polanyi and Welke, *ibid.*, 1928, **132A**, 371.

²² Threlfall, *Phil. Mag.*, 1887, **23**, 223.

²³ Adwentosky, *Bull. Acad. Cracow*, 1902, 742.

Summary.

1. The adsorption of ten gases on sodium chloride crystals at low temperatures and pressures has been investigated.
2. The surface is very sensitive to impurities and to variations in the conditions of outgassing.
3. Dipole gases are highly adsorbed according to the value of their electric moment; there is a parallelism between the adsorbability of non-polar gases and their polarisability.
4. The shape of the isotherms are qualitatively explained by assuming that there are forces operating between adsorbed molecules. Association of nitric oxide occurs in the surface layer, and carbon dioxide lies flat on the surface when adsorbed.
5. The heats of adsorption of argon and methane and carbon monoxide in the temperature range $-183^{\circ}\text{C}.$ — $-192^{\circ}\text{C}.$ are much smaller than anticipated from theoretical considerations.
6. There is no lateral diffusion of adsorbed molecules at $-192^{\circ}\text{C}.$ or at $-183^{\circ}\text{C}.$, but a slow secondary absorption is found at $-78.2^{\circ}\text{C}.$

The author wishes to express his thanks to Professor W. E. Garner and to Professor A. J. Allmand for constant interest and advice during the course of the investigation; and also to the Dept. of Scientific and Industrial Research for a maintenance grant and to the Imperial Chemistry Industries for a grant for the purchase of apparatus.

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NOTE ON THE SURFACE TENSION OF SOAP SOLUTIONS.

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Most of the recorded observations on the surface tension of soap solutions are on carefully neutralised solutions. The results of different workers, and even of the same worker under slightly different conditions, are not very concordant, and Lottermoser and his co-workers¹ have found that carbon dioxide in the air causes a slow decrease in tension, in some solutions, and that the nature and treatment of the glass vessels containing the solutions affects the tension. He ascribes this to hydrolysis of the soap, and concludes that it is very difficult to obtain reproducible results for the surface tension of soap solutions. A change in the small amount of hydrolysis in the interior may be expected to produce a very considerable change in the equilibrium between interior and surface, if the free acid, or acid soap, produced by hydrolysis is much more strongly adsorbed than the neutral soap. Since the COOH

¹ *Trans. Faraday Soc.*, 1935, **31**, 200; *Kolloid-Z.*, 1935, **73**, 155, 270; *Kolloid-Beihfte*, 1935, **51**, 73.

group has a much smaller attraction for water than COONa , it is to be expected that free acid will be more strongly adsorbed than neutral soap. It has, moreover, been shown, by analysis of the foam on soap solutions, by Perrin,² Miss Laing,³ and Laing, McBain and Harrison,⁴ that the soap present in the surface layer of neutral soap solutions contains a large excess of acid; that obtained from a slightly alkaline solution is, however, neutral.

The effect of the addition of small amounts of alkali to soap solutions, on the surface tension, can also be explained if the free acid, or acid soap, produced by hydrolysis, is much more strongly adsorbed than the neutral soap. Harkins and Clark,⁵ Ekwall,⁶ and Powney⁷ found that the tension of "neutral" soaps is of the order 20-25 dynes per cm., this tension remaining practically unchanged (with a soap of twelve or more carbon atoms) as the concentration increased from $N/500$ upwards. Addition of a very small amount of alkali increases the surface tension very rapidly, to a maximum which is about 62 dynes per centimetre for a $N/500$ potassium laurate solution, but decreases as the solution becomes more concentrated. Rather more alkali must be added to reach this maximum of tension, the stronger the solution of soap, but the amounts required are quite small. If alkali is added in quantities much greater than that necessary to reach the maximum of tension, the tension decreases slowly and almost linearly with increasing alkali concentration; but it always remains far above the tension of a neutral soap solution.

Qualitatively, the very low tension found with the "neutral" solutions is that appropriate to a solution with a surface layer practically saturated with adsorbed molecules; as the tension is very much raised on adding a little alkali, which suppresses hydrolysis, the adsorbed layer is probably mainly acid or acid soap. The maxima of tension probably occur where the alkali is just sufficient to suppress hydrolysis practically completely; more alkali has to be added to the stronger solutions to reach these maxima because more is needed to suppress the hydrolysis. The equilibrium between interior and surface now concerns neutral soap molecules only, and the surface is not nearly saturated at $N/500$ nor is it completely saturated even at $N/50$.

A close approximation to the true surface tension-concentration curve for a solution containing no capillary active molecules except neutral soap is probably given by plotting the maxima of curves such as those given by Powney^{*} against the concentration of soap (potassium laurate). From the surface tension-concentration data the state of the adsorbed film may be deduced by Gibbs' adsorption equation. In the table, the molar concentration m , the activity coefficient f , given by Randall, McBain and White⁸ (interpolated as for a dilute uni-univalent electrolyte), the depression of surface tension F , given by Powney, the adsorption Γ calculated by Gibbs' equation from the slopes of the smoothed curve relating F to $\log fm$, and the area per molecule in the adsorbed film, are given.

² *Ann. Physique*, 1918, 10, 182.

⁵ *Proc. Roy. Soc.*, 1925, 109A, 28.

⁴ 6th Colloid Symposium Monograph, 1928, 63.

³ *J. Amer. Chem. Soc.*, 1925, 47, 1854.

⁷ *Acta Acad. Aboensis (Math. Phys.)*, 1927, 4, 6.

⁶ *Trans. Faraday Soc.*, 1935, 31, 1510.

^{*} Fig. 6, p. 1517 of paper cited.

⁸ *J. Amer. Chem. Soc.*, 1926, 48, 2517.

ADSORPTION OF NEUTRAL POTASSIUM LAURATE MOLECULES.

Concentration (Moles per Litre), <i>m</i> .	Activity Coefficient, <i>f</i> .	Depression of Surface Tension, <i>F</i> .	Absorption: Molecules per Sq. Cm., <i>Γ</i> .	Area per Molecule, Sq. Å., <i>A</i> .
0.0021	0.95	11.1	2.59×10^{14}	38.6
0.0042	0.93	19.8	2.92 ..	34.3
0.0084	0.90	25.9	3.13 ..	31.9
0.0126	0.88	30.7	3.46 ..	28.9
0.021	0.85	38.2	3.78 ..	26.5

The relation between *F* and *A* is that of a typical "gaseous" film under rather high surface pressure. The surface is not completely saturated even at the highest of the concentrations here measured.

The slow decrease in surface tension observed when much larger amounts of alkali are added is perhaps due to incipient salting out of the soap; it would be interesting to see whether neutral salts produce the same effect as the alkali added in excess of the amount required to reach the maximum of tension.

The fact that the tension in neutral solutions at concentrations as low as $N/500$ has reached the minimum of 22 dynes per centimetre indicates that the acid, or acid soap, is exceedingly strongly adsorbed.

Assuming the usual formula for the fraction hydrolysed, $\sqrt{\frac{k_w}{mk_a}}$, and taking the dissociation constant k_a of lauric acid as 1.4×10^{-5} , the concentration of undissociated lauric acid in the interior of the $N/500$ soap should be about 1.2×10^{-6} *N*. A solution of lauric acid in water containing this concentration of undissociated acid would have a total concentration of 5.3×10^{-6} *N*, if the above dissociation constant is assumed.

Frumkin's data⁹ on the surface tension of solutions of lauric acid give, at 18°, a depression of about 22.5 dynes per centimetre in water for this concentration. This is smaller than the change in surface tension (about 40 dynes) caused by suppressing hydrolysis in $N/500$ potassium laurate; but Frumkin also says that very much greater depressions of tension were obtained if the lauric acid solutions had their surfaces contracted just before taking the measurements; moreover his method of measurement, withdrawing a vertical thin plate from the surface, would be likely to extend the surface, reducing the surface concentration of the adsorbed molecules, which would be but slowly made up in these very dilute solutions; there is a probability that his results for the tension are too high and for the depression of tension too low. At any rate, it can be said that the amount of acid produced by hydrolysis in a "neutral" soap solution would be expected to produce a very large lowering of surface tension.

The very great magnification of hydrolysis in the surface layer, due to the much greater surface activity of the acid over that of the soap, renders experiments on the surface properties of "neutral" soap solutions liable to unexpected errors. It would therefore appear desirable, in measuring any surface properties of soap solutions, to add sufficient alkali to suppress hydrolysis, or at any rate to take very great care that the p_H of the solution is exactly controlled.

⁹ *Z. physikal. Chem.*, 1925, 116, 482.

Summary.

The effects of slight traces of alkali in raising the surface tension of soap solutions are explained as due to suppression of hydrolysis, which is very much magnified in the surface layers, since the surface activity of the acid, or acid soap, is very much greater than that of neutral soap. The adsorption of neutral potassium laurate is calculated from published data, and the adsorbed film is found to be gaseous, of the usual type.

I am indebted to Mr. G. S. Hartley for helpful discussion.

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THE KINETICS OF POLYMERISATION PROCESSES. PART II.

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In an earlier paper¹ the kinetics of polymerisation processes was discussed, and reasons were advanced for the view that in many cases a steric factor is the important factor in controlling the size of the final polymer. A similar view has been put forward by Bawn,² while Dostal and Mark³ do not consider that the steric factor can be much affected by chain length. It is perhaps necessary to point out here that the definition of "steric factor" employed in Part I. leads to an unusual interpretation of the reaction velocity constants. The equations are there derived in terms of the number of molecules n_r of the polymer M_r , reckoned in terms of the monomer, so that n_r is proportional to the mass of M_r and the velocity constant k_r (for the addition of M to M_r) is thus defined in terms of the masses of the reactants. To transform from this system to the more conventional one which employs molecular concentration it is clearly necessary to introduce a factor $1/r$. The net result of carrying out this process is to multiply the steric factor by r , so that the equations given in Part I. for a process with a steric factor $1/r$ are strictly comparable with those derived by Dostal and Mark.³ By the introduction of a function Z termed the *Eigenzeit* these authors were able to give a rigid integration of the differential equations set up for the concentrations of the various polymers, and to obtain expression for these concentrations in terms of Z . As Z is not directly measurable their results are not immediately applicable to experiment and it therefore appears desirable to give here a few notes on the relationship between the results of the two methods of analysis before proceeding to discuss other polymerisation mechanisms.

¹ Gee and Rideal, *Trans. Faraday Soc.* 1935, **31**, 969.

² Bawn, *ibid.*, 1936, **32**, 178.

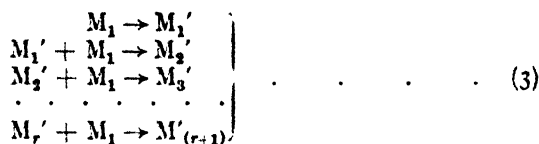
³ Dostal and Mark. (a) *Z physik. Chem.* 1935, **29B**, 299; (b) *Trans. Faraday Soc.*, 1936, **32**, 54.

In this paper we shall modify slightly the nomenclature of Part I. since it will be necessary to distinguish between active and inactive polymers. We shall therefore denote the various inactive molecular species by $M_1, M_2, M_3, \dots, M_r, \dots$; the corresponding active bodies by $M_1', M_2', M_3', \dots, M_r', \dots$; and their concentrations (in terms of monomer) by $n_1, n_2, \dots, n_r, \dots$; $n_1', n_2', \dots, n_r', \dots$ respectively. If n_0, N are respectively the numbers of molecules present initially and at time t , then obviously

$$n_0 = (n_1 + n_1') + (n_2 + n_2') + \dots + (n_r + n_r') + \dots \quad (1)$$

$$N = (n_1 + n_1') + \frac{1}{2}(n_2 + n_2') + \dots + \frac{1}{r}(n_r + n_r') + \dots \quad (2)$$

In the case so far discussed the only inactive body present is M_1 , so that $n_2 = n_3 = \dots = n_r = 0$, and the reaction is represented by:



The velocity constant of the activation reaction is $\alpha k n_0$ as before; the other reactions all have a velocity constant K (in terms of concentrations), so that we have

$$\left. \begin{array}{l} -\frac{dn_1}{dt} = K n_1 \left(\alpha n_0 + n_1' + \frac{1}{2} n_2' + \dots + \frac{1}{r} n_r' + \dots \right) \\ \frac{dn_1'}{dt} = K n_1 (\alpha n_0 - n_1') \\ \vdots \\ \frac{dn_r'}{dt} = r K n_1 \left(\frac{n_{r-1}'}{r-1} - \frac{n_r'}{r} \right) \end{array} \right\} \quad (4)$$

We now introduce the function Z , defined by

$$Z = K \int_0^t n_1 dt \quad (5)$$

This differs from Dostal and Mark's definition by the factor K , and thus obviates the dimensional difficulties of their paper by making it clear that Z is a pure number. In a similar way, Dostal and Marks constant " a " is replaced here by αn_0 where α is unambiguously a fraction. It can then be shown* that

$$\frac{1}{r} n_r' = \alpha n_0 e^{-Z} \sum_{r=1}^{\infty} \frac{Z^r}{r!} \quad (6)$$

$$n_1 = n_0 (1 - \alpha Z - \frac{1}{2} \alpha Z^2) \quad (7)$$

$$N = n_0 (1 - \frac{1}{2} \alpha Z^2) \quad (8)$$

* The derivation follows the method of Dostal and Mark; the slight change in equation (6) arises because these authors have made the unnecessary approximation of putting $\frac{dn_1'}{dt} = 0$.

It was shown in Part I. that the mean chain length ν of the polymerised fraction is given by :

$$\nu = \frac{n_0 - n_1}{N - n_1} \quad (9)$$

and combining with (7) and (8) we find

$$\nu = 1 + \frac{1}{2}Z \quad (10)$$

so that Z is approximately equal to twice the mean chain length of the polymerised fraction.

Combining these results with those of Part I. it is easily shown that the reaction velocity is given by :

$$-\frac{dN}{dt} = 2\alpha K n_0 \left[N \left\{ 1 + \sqrt{\frac{n_0 - N}{2\alpha n_0}} \right\} - n_0 \right] \quad (11)$$

or in terms of the fraction polymerised $x \left(= 1 - \frac{n_1}{n_0} \right)$

$$\frac{dx}{dt} = \alpha K n_0 (1 - x) \sqrt{1 + \frac{2x}{\alpha}} \quad (12)$$

while the mean chain length ν is found to be

$$\nu = 1 + \sqrt{\frac{n_0 - N}{2\alpha n_0}} \quad (13)$$

By differentiation of (11) it is easily shown that the condition for the velocity to be a maximum is

$$\left(\frac{N}{n_0} \right)_{\max.} = \frac{2}{3} - \frac{4\alpha}{9} \left\{ 1 - \sqrt{1 + \frac{3}{2\alpha}} \right\} \quad (14)$$

This means that for any probable value of α the maximum occurs when about one-third of the material has been polymerised, so that the suggestion advanced in Part I. that the observed shift of the position of this maximum is to be attributed to the size of the final polymer requires modification. We shall return to this point later, but we may discuss here the case where the maximum occurs after more than $\frac{1}{2}$ polymerisation. By an extension of the methods of Part I. it is easily shown that the velocity of a polymerisation chain in which the constants of the successive stages (after the first) decrease according to the law

$$k_r = \frac{K}{r^p} \quad (15)$$

is given approximately by

$$-\frac{dN}{dt} = \frac{K}{\nu^p(\nu - 1)^2} (N\nu - n_0)(n_0 - N) \quad (16)$$

so that the condition for the $\left(\frac{dN}{dt} \sim N \right)$ curve to become parabolic is $\nu \rightarrow \text{const.}$, a condition which will be fulfilled for reactions in which a large steric factor is operative.

We now propose to consider some cases in which other methods of chain termination become important. It is evident that if the rate of propagation of the polymerisation chains is large compared with the rate of initiation, any factor which tends to deactivate the growing

polymer will become of great importance, and we may thus divide polymerisation processes roughly into three groups:

(i) The type already considered where the steric factor exerts the controlling influence on chain length.

(ii) Cases where the ratio of propagation rate to initiation rate is so large that the chain length is governed almost entirely by factors leading to deactivation.

(iii) Intermediate cases where both mechanisms play comparable parts.

A qualitative discussion of the various mechanisms which may lead to deactivation has been given by Rideal,⁴ and the view that such a variety of processes may—under different circumstances—play an important part is supported by the apparent complexity of the phenomena described by the workers taking part in the recent Faraday Society General Discussion.⁵ The quantitative application of these ideas has been commenced by Melville,⁶ in a study of the photopolymerisation of acetylene and by Norrish and Carruthers,⁷ who have investigated the thermal polymerisation of formaldehyde in the presence of formic acid. In the following pages we shall discuss the behaviour of polymerisation processes in which the growth of the chains is terminated in various ways, and consider the application of the results to experiment.

Case II. The Chains are Terminated by "Spontaneous" Deactivation.

Under this heading we may include any mechanism which is independent of collisions with other reactants, such as a reversion of the active group to a stable inactive form, or the collision of an active group with the wall.

The growth of the polymer is represented as before by reactions (3), while its termination occurs by:



The velocity constants of these reactions (17) we shall assume to be constant and to be related to those of reactions (3) by the factor λn_0 :

$$k_r = K \cdot \lambda n_0 \quad (18)$$

The rates of formation of the various molecular species can now be written down and the total rate of reaction obtained by the relationship

$$\frac{dN}{dt} = \frac{d}{dt}(n_1 + n_1') + \frac{1}{2} \frac{d}{dt}(n_2 + n_2') + \dots + \frac{1}{r} \frac{d}{dt}(n_r + n_r') + \dots \quad (19)$$

A simplification can be made at this point, since our discussion is to be confined to cases where the rate of chain initiation is small compared with the rate of termination ($\alpha \ll \lambda$) and the chain length is thus

⁴ Rideal, *Trans. Faraday Soc.*, 1936, **32**, 3.

⁵ General Discussion on Polymerisation, *ibid.*, 1936, **32**, 1-412.

⁶ Melville, *ibid.*, 1936, **32**, 258; cf. also Rideal, *P.R.S.*, 1934, **146A**, 268.

⁷ Norrish and Carruthers, *Trans. Faraday Soc.*, 1936, **32**, 195.

governed by the latter process. It is therefore permissible to write stationary state equations for the concentrations of all the active bodies involved, so that (19) reduces to:

$$\frac{dN}{dt} = \frac{dn_1}{dt} + \frac{1}{2} \frac{dn_2}{dt} + \dots + \frac{1}{r} \frac{dn_r}{dt} + \dots \quad (20)$$

It is easily seen from (3) and (17) that, for $r \geq 2$

$$\frac{dn_r}{dt} = K n_r' \cdot \lambda n_0 \quad (21)$$

$$\frac{dn_1}{dt} = K \left[\lambda n_0 n_1' - \alpha n_0 n_1 - n_1 \left(n_1' + \frac{1}{2} n_2' + \dots + \frac{1}{r} n_r' + \dots \right) \right] \quad (22)$$

$$\text{whence} \quad \frac{dN}{dt} = -K n_1 \left[\alpha n_0 + \left(1 - \frac{\lambda n_0}{n_1} \right) \sum_{r=1}^{\infty} \frac{1}{r} n_r' \right] \quad (23)$$

To evaluate $\sum_r n_r'$ we write down the stationary state equations for all the active bodies, and sum:

$$\left. \begin{aligned} \frac{dn_1'}{dt} &= 0 & \therefore \alpha n_0 n_1 &= n_1' (n_1 + \lambda n_0) \\ \frac{dn_2'}{dt} &= 0 & \therefore n_1 n_1' &= \frac{1}{2} n_2' (n_1 + \lambda n_0) \\ &\vdots & & \\ \frac{dn_r'}{dt} &= 0 & \therefore \frac{1}{r-1} n_1 n_{r-1}' &= \frac{1}{r} n_r' (n_1 + \lambda n_0) \\ &\vdots & & \end{aligned} \right\} \quad (24)$$

$$\text{Adding} \quad \alpha n_0 n_1 + n_1 \sum_{r=1}^{\infty} \frac{1}{r} n_r' = (n_1 + \lambda n_0) \sum_{r=1}^{\infty} \frac{1}{r} n_r'$$

$$\text{whence} \quad \sum_{r=1}^{\infty} \frac{1}{r} n_r' = \frac{\alpha}{\lambda} n_1 \quad (25)$$

Combining this equation with (23) we find

$$-\frac{dN}{dt} = \frac{\alpha}{\lambda} K n_1^2 \quad (26)$$

or, in terms of x ,

$$\frac{dx}{dt} = \frac{\alpha}{\lambda} K n_0 (1-x)^2 \left(\frac{1+2\lambda-x}{1+\lambda-x} \right) \quad (26a)$$

We next wish to know how the mean chain length ν of the polymerised fraction varies during the reaction. We have, by differentiation of equation (9)

$$-\frac{d\nu}{dn_1} = \frac{\nu}{n_0 - n_1} - \frac{\nu^2}{n_0 - n_1} \left(1 - \frac{dN}{dn_1} \right) \quad (27)$$

$$\text{Then} \quad 1 - \frac{dN}{dn_1} = 1 - \frac{dN/dt}{dn_1/dt} = \frac{\lambda n_0}{n_1 + 2\lambda n_0} \quad (28)$$

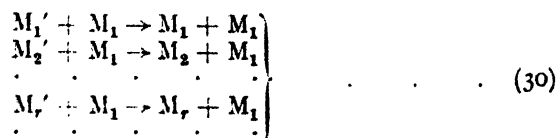
Substituting from (28) in (27) and integrating we obtain finally

$$\nu = \frac{n_0 - n_1}{\lambda n_0 \ln \left\{ \frac{n_0 + 2\lambda n_0}{n_1 + 2\lambda n_0} \right\}} \quad (29)$$

Case III. The Chains are Terminated by Collision with a Molecule of Monomer.

Analysis of the kinetic data obtained in the photopolymerisation of acetylene has been shown by Melville⁶ to lead to the conclusion that collision between a growing polymer and a molecule of monomer may lead either to chain growth or deactivation, and a similar mechanism has been found by Norrish and Carruthers⁷ to be operative in the polymerisation of formaldehyde. It would thus appear that this may be a mechanism which is frequently of importance, and we shall now proceed to a kinetic analysis.

Chain growth is represented as before by (3), but (17) must be replaced by



The velocity constant of any of these reactions (assumed the same) is given by

$$k_r'' = \gamma \cdot K \quad (30a)$$

where γ is a constant.

The analysis follows exactly the same lines as before, and it is found that

$$-\frac{dN}{dt} = \frac{\alpha K n_0 n_1}{\gamma} \quad (31)$$

or, in terms of x ,

$$\frac{dx}{dt} = \frac{\alpha(1 + 2\gamma)}{\gamma(1 + \gamma)} K n_0 (1 - x) \quad (31a)$$

$$v = 2 + \frac{1}{\gamma} \quad (32)$$

This last equation is identical with the result found by Melville.

Case IV. Partial Deactivation.

In Cases II. and III. we have assumed that the size of the polymer is controlled completely by the deactivation process, while case I. on the other hand neglects this entirely. It is clear that intermediate cases must exist and indeed are probably very general. The problem now becomes much more difficult since no stationary state equations can be employed, but by making use of the "Z" function (equation (5)) the mechanism of Case III. can be re-investigated, as follows:

It is easily shown that

$$-\frac{dN}{dZ} = n_1' + \frac{1}{2}n_2' + \frac{1}{3}n_3' + \dots \quad (33)$$

where the various terms are given by

$$\left. \begin{aligned} \frac{dn_1'}{dZ} &= \alpha n_0 - (1 + \gamma)n_1' \\ \frac{1}{2} \frac{dn_2'}{dZ} &= n_1' - \frac{1}{2}(1 + \gamma)n_2' \\ \vdots &\vdots \\ \frac{1}{r} \frac{dn_r'}{dZ} &= \frac{n_{r-1}'}{r-1} - \frac{1 + \gamma}{r} n_r' \end{aligned} \right\} \quad (34)$$

whence

$$\frac{1}{r} n_r' = \frac{\alpha n_0}{(1+\gamma)^r} \left[1 - \left\{ 1 + Z(1+\gamma) + \frac{Z^2}{2}(1+\gamma)^2 + \dots + \frac{Z^{r-1}}{(r-1)!}(1+\gamma)^{r-1} \right\} e^{-(1+\gamma)Z} \right] \quad (35)$$

Combining equations (33) and (35) and summing to $r \rightarrow \infty$

$$-\frac{dN}{dZ} = \frac{\alpha n_0}{\gamma(1+\gamma)} (1 - e^{-\gamma Z}) \quad (36)$$

whence
$$n_0 - N = \frac{\alpha n_0}{\gamma(1+\gamma)} \left\{ Z - \frac{1}{\gamma}(1 - e^{-\gamma Z}) \right\} \quad (37)$$

Similarly
$$-\frac{dn_1}{dZ} = \frac{\alpha n_0}{\gamma} \left(1 - \frac{e^{-\gamma Z}}{1+\gamma} \right) \quad (38)$$

Polymerisation with Spontaneous Deactivation.
 $I, II, \lambda = 0.01$
 $I, \beta \frac{\alpha}{n_0} = 0.01$ [Cf. part II]

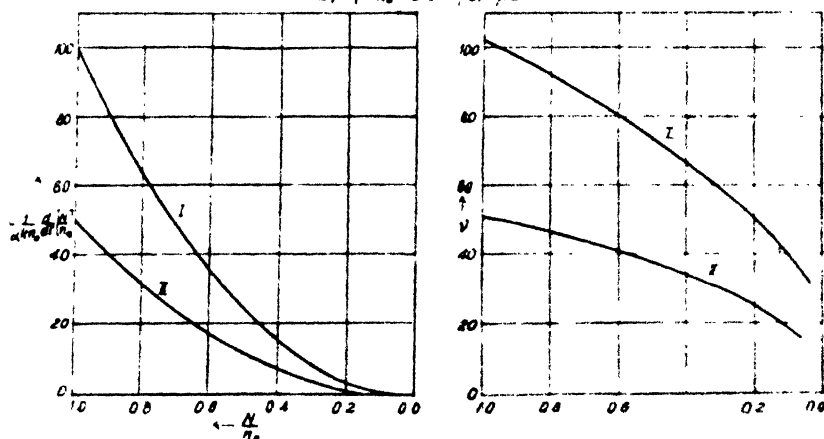


FIG. 1.

and
$$n_0 - n_1 = \frac{\alpha n_0}{\gamma} \left\{ Z - \frac{1}{\gamma(1+\gamma)} (1 - e^{-\gamma Z}) \right\} \quad (39)$$

Subtracting (39) from (37) and dividing into (39) we can find the chain length ν from equation (9). The result is

$$\nu = \frac{1+\gamma}{\gamma} \left\{ 1 - \frac{1 - e^{-\gamma Z}}{Z\gamma(1+\gamma)} \right\} \quad (40)$$

Equations (36) and (38) can now be combined with (5) to give the velocity of polymerisation as a function of Z :

$$-\frac{dN}{dt} = \frac{\alpha K n_0 n_1}{\gamma(1+\gamma)} (1 - e^{-\gamma Z}) \quad (41)$$

$$\frac{dx}{dt} = \frac{\alpha K n_0^2}{\gamma} (1-x) \left(1 - \frac{e^{-\gamma Z}}{1+\gamma} \right) \quad (42)$$

By further differentiation the condition for the velocity to be a maximum

is:
$$2e^{-2\gamma Z} - \left\{ 3 + \gamma + \gamma(1+\gamma) \left(\frac{\gamma}{\alpha} - Z \right) \right\} e^{-\gamma Z} + (1+\gamma) = 0 \quad (43)$$

These equations (5, 36-43) give a complete description of the behaviour of the system in terms of the parameter Z .

Polymerisation with Deactivation by Monomer

I, II, $\gamma = 0.01$

$\beta \beta_0 = 0.01$ (cf part III)

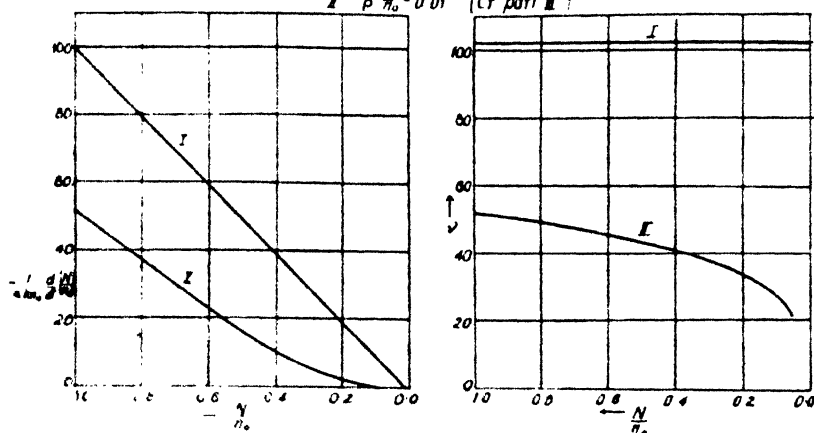


FIG. 2.

Polymerisation with Partial Deactivation by Monomer.

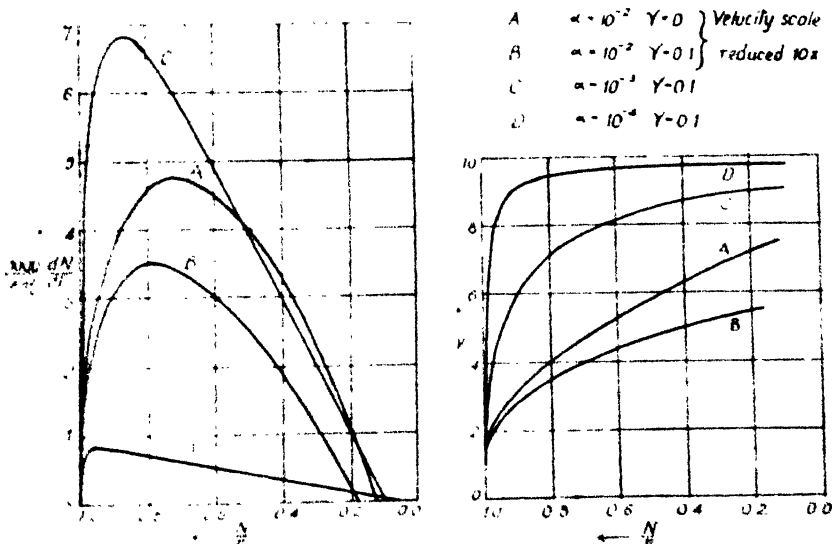


FIG. 3.

Summary of Results and Experimental Application.

In Figs. 1 to 3 are given plots of the velocity and chain length as functions of N/n_0 for the various mechanisms discussed above.* These curves have been derived from the theoretical equations as follows:

* Figs. 1 and 2 include also curves showing the effects of inhibitors. The equations on which these are based are derived in Part III. (below).

Figs. 1 and 2.—For a given value of n_1 , dN/dt is calculated from equations (26), (31) and ν from (29) and (32) while the corresponding values of N are found from (9) by putting in the derived values of ν .

Fig. 3.—Curves A are obtained directly from equations (11), (13). Curves B, C, D are obtained by calculating dN/dt , ν and N for given values of Z by means of equations (41), (40), (37).

The principal features of the different curves will be evident on inspection. When deactivation is the controlling factor of the process the induction period vanishes* and the curve becomes pseudo bimolecular (spontaneous deactivation) or unimolecular (deactivation by monomer) while the mean chain length remains constant in the latter case and decreases during the reaction in the former. In all the curves of Fig. 3 an induction period is evident, and the chain length of the polymer increases progressively. In these curves we may note further that the fraction polymerised before the maximum velocity is attained decreases progressively as the deactivation reaction becomes increasingly important. We have thus a complete explanation of the variation of induction period from zero (strong deactivation) to $\frac{1}{2}$ reaction (no deactivation; no steric factor) and finally to $\frac{1}{2}$ reaction (large steric factor).

We may now turn to consider the application of these results, and we note first that we can measure experimentally:

1. The velocity of polymerisation.
2. The mean chain length of the polymer at various stages of reaction.
3. Possibly also the distribution of molecular sizes in the polymer.†

From 1 we can plot a gradient curve ($\frac{dN}{dt} \sim N$) and thence obtain

- (a) the position and magnitude of maximum velocity;
- (b) if the induction period is short or absent the shape of the later part of the curve, and thence a uni- or bi-molecular constant.

These observations suffice to enable us to decide by inspection what mechanism is operative, and thus by application of the equations given above to obtain the values of the various constants. The procedure may be illustrated by reference to specific examples taken from published work:

1. It is scarcely surprising to find no completely satisfactory example of the simplest Case I. (no deactivation; zero steric factor) although Dostal and Mark^{2(b)} have shown that some rather fragmentary data for the early stages in the polymerisation of styrene can be adequately represented by this type of curve, but since the chain length has not been measured we cannot find α and Kn_0 separately. From the published curve (Fig. 9) $\left(\frac{dx}{dt}\right)_{\max.}$ is about 1.8, and putting $x_{\max.} = \frac{1}{2}$ it is easily found that

$$Kn_0\sqrt{\alpha} \cong 3.2.$$

* This, of course, is not strictly true. It is more accurate to say that the induction period is too short to be detected experimentally.

† Cf. Schultz, *Z. physik. Chem.*, 1935, **30B**, 379. It should be pointed out that the distribution depends on the mechanism, and Schultz' calculation is therefore only valid for the special mechanism he considers. His results may be compared for ex. with the curves given by Dostal and Mark² and Carothers (*Trans. Faraday Soc.*, 1936, **32**, 39).

2. Numerous examples of reactions in which $x_{\max.} > \frac{1}{2}$ are given by polymerisation of monolayers of oxidised maleic anhydride β -eleostearin.⁸ It is probably best in these cases to adhere to the proposal to describe such reactions by the Semenoff equation (*cf.* ref. 8 and Part I.).

3. Examples of pseudo bimolecular reactions, which we can interpret as showing spontaneous deactivation, are given by the polymerisation of indene⁹ and $\beta\gamma$ dimethyl butadiene.¹⁰ In both cases a short induction period is found, the maximum occurring after about 18 per cent. polymerisation in the former case, 12 per cent. in the latter; the respective bimolecular constants (in $\text{secs.}^{-1}/\text{per cent.}$) being 1.8×10^{-8} ; 1.25×10^{-5} . These measure $\alpha K/\lambda$ but as the general case of spontaneous deactivation with an induction period has not been worked out, we cannot determine these three constants separately.

Polymerisation of Isosafrole at 258°C [Whitby & Katz].

◦ *Experimental Points*

A. Calculated from $\alpha = 5.7 \times 10^{-1}$, $\gamma = 0.2$, $K\eta_0 = 2.2 \times 10^{-6} \text{secs.}^{-1}$

B. Unimolecular Constant $5.7 \times 10^{-6} \text{secs.}^{-1}$ Chalmers.

C. Zero steric factor; no deactivation $\alpha = 2.5 \times 10^{-6}$; $\gamma = 0$.

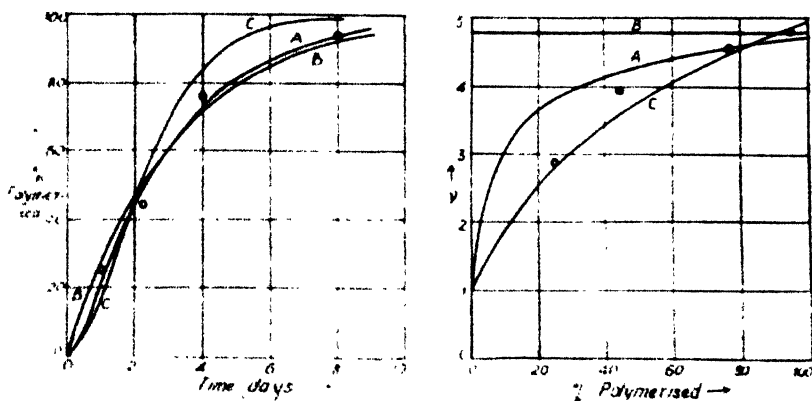


FIG. 4.

4. Chalmers¹¹ has collected the results of a number of polymerisation reactions which appear to be pseudo-unimolecular, and although a closer examination shows some of these to be better represented by other types of equation, there remain several examples of this type (deactivation by monomer). Among these may be mentioned the thermal¹² and photo¹³ polymerisation of vinyl acetate, for which the velocity constants are respectively 1.83×10^{-5} (at 82° C.) and 5.8×10^{-5} . For the latter case the quantum efficiency and inhibitory effect of pyrogallol suggest a chain length of the order of 1000, so that $\gamma \cong 10^{-3}$, and $(\alpha K\eta_0) \cong 6 \times 10^{-8}$.

⁸ Gee and Rideal, *P.R.S.*, 1935, **153A**, 116; Gee, *ibid.*, p. 129; *Trans. Faraday Soc.*, 1936, **32**, 187.

⁹ Whitby and Katz, *J.A.C.S.*, 1928, **50**, 1160.

¹⁰ Lebedeff, *J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1313.

¹¹ Chalmers, *J.A.C.S.*, 1934, **56**, 912.

¹² Starkweather and Taylor, *ibid.*, 1930, **52**, 4708.

¹³ Jeu and Alyea, *ibid.*, 1933, **55**, 575.

5. An example of a reaction in which a short induction period is followed by a pseudo-unimolecular curve appears to be given by isosafrole,¹⁴ for which Whitby's data is well represented by curves calculated from the constants $\alpha = 3.7 \times 10^{-3}$; $\gamma = 0.2$; $Kn_0 = 2.2 \times 10^{-4}$ secs.⁻¹. γ is estimated from the final chain length, for it is easily seen from (40) that if Z_∞ is large

$$v_{\infty} \approx \frac{1}{\gamma} \quad . \quad . \quad . \quad . \quad . \quad (44)$$

α and Kn_0 are then deduced from the height and position of the maximum of the velocity curve. In Fig. 4 the fit given by this curve is compared with that for a simple unimolecular law (Chalmers¹¹) or the no deactivation mechanism (Case I.). Considering both velocity and chain length this analysis is definitely the best, while if—as might well be the case—the “polymer” sample after one day contained a small amount of monomer, the experimental points would lie still nearer to the theoretical curve.

Summary.

The discussion of the kinetics of a polymerisation chain is continued and extended to cases where chain breaking mechanisms are operative. Those considered include spontaneous deactivation and deactivation by a special type of collision with the monomer. It is shown that the fraction polymerised before the maximum velocity is attained varies from zero with strong deactivation to one-third with no deactivation and zero steric factor and finally approaches a half for large steric factors.

The application of this analysis to experimental measurements is discussed and actual examples of the various mechanisms are quoted from the literature.

The author's thanks are due to Professor E. K. Rideal for many valuable discussions, and to the Imperial Chemical Industries (Dyestuffs Group) for financial aid.

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¹⁴ Whitby and Katz, *Can. J. Res.*, 1931, 4, 487.

THE KINETICS OF POLYMERISATION PROCESSES. PART III. THE EFFECTS OF CATALYSTS AND INHIBITORS.

BY GEOFFREY GEE AND ERIC K. RIDEAL.

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The effect of inhibitors on the rate of a polymerisation reaction is well known, and quantitative studies of the phenomenon have been made by Jeu and Alyea,¹ and by Taylor and Vernon.² The measurements of the latter workers are unfortunately complicated by the fact that the inhibitors they employed absorbed a part of the radiation which was

¹ Jeu and Alyea, *J.A.C.S.*, 1933, **55**, 575.

¹ Taylor and Vernon, *ibid.*, 1931, 53, 2527.

initiating the reaction chains. Jeu and Alyea, although also studying photo-polymerisation, avoided this difficulty by employing a band of the spectrum which was not absorbed by the inhibitors they investigated.

Empirically, their results can be expressed in the form: $k = \frac{k_0}{1 + \alpha c}$,

where k_0 is the velocity constant in the absence of inhibitor,

k is the velocity constant when the inhibitor concentration is c ,

α is a specific constant for the inhibitor.

On the analogy of the Christiansen-Kramers energy chain, this was written in the form:

$$k = \frac{k_1 k_2}{k_3 + k_4 c}$$

where k_1 , k_2 , k_3 and k_4 are the respective velocity constants for initiation, propagation, spontaneous termination, and inhibition of the chains. Jeu and Alyea then proceeded further to estimate the chain length ν , assuming by analogy that this was given by:

$$\nu = \frac{k_2}{k_3 + k_4 c}$$

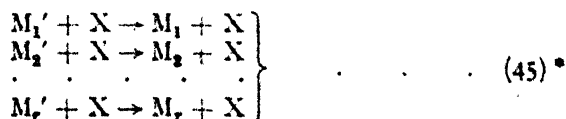
The problem has been discussed by Chalmers,³ and the same form of equation deduced by a simple argument based on a stationary state equation for the activated monomer in a polymerisation chain. Chalmers arrived at the conclusion that $\frac{k_2}{k_3 + k_4 c}$ is to be interpreted, not as the chain length of the polymer, but as the mean life of the activated monomer. Unfortunately, his derivation neglects entirely the effect of the inhibitor on the activated polymeric molecules, and provides no mechanism of chain termination, so that its physical basis is doubtful.

Notwithstanding the many interesting features exhibited by catalysed polymerisation processes there would appear to be as yet no reliable quantitative data for the effect of catalysts on polymerisation velocity, while the mechanism of catalysis remains a matter of dispute. Qualitative and semi-quantitative observations reveal wide differences of behaviour between different types of catalytic polymerisation, and no general explanation of the phenomenon has yet been given.

In this paper we shall investigate the effects of inhibitors and catalysts on polymerisation processes proceeding by mechanisms discussed in Part II. (above).

I. Inhibitors.

We consider a polymerisation chain whose growth is described by equation (3) of Part II.; the termination of the chain by an inhibitor X may then be represented by:



* Chalmers, *J.A.C.S.*, 1934, **56**, 912.

* The numbering of the equations is continued from Part II. to facilitate reference. These equations assume that the inhibitor does not undergo chemical change during the deactivation process.

The velocity constants k_r''' of these reactions are assumed to be the same, and are given by :

$$k_r''' = K \cdot \beta \quad . \quad . \quad . \quad (46)$$

where β is a constant.

If the number of molecules of inhibitor present is c its concentration is c/n_0 moles/mole of polymerisable material.

We are now in a position to examine the effect of introducing this additional chain-breaking mechanism to reactions in which the normal mechanism of deactivation is spontaneous (Case II.) or collision with monomer (Case III.). The revised equations for the velocity and polymer size are found to be :

Case II., Spontaneous Deactivation. (Cf. equations (26), (29).)

$$-\frac{dN}{dt} = \frac{\alpha K n_0 n_1^2}{\lambda n_0 + \beta c} \quad . \quad . \quad . \quad (47)$$

$$v = \frac{n_0 - n_1}{(\lambda n_0 + \beta c) \ln \left\{ \frac{n_0 + 2(\lambda n_0 + \beta c)}{n_1 + 2(\lambda n_1 + \beta c)} \right\}} \quad . \quad . \quad (48)$$

Case III., Collision with Monomer. (Cf. equations (31), (32).)

$$-\frac{dN}{dt} = \frac{\alpha K n_0 n_1^2}{\gamma n_1 + \beta c} \quad . \quad . \quad . \quad (49)$$

$$v = \frac{(1 + 2\gamma)(n_0 - n_1)}{\gamma \left[(n_0 - n_1) + \frac{\beta c}{\gamma(1 + 2\gamma)} \ln \left\{ \frac{n_0 + \frac{2\beta c}{1 + 2\gamma}}{n_1 + \frac{2\beta c}{1 + 2\gamma}} \right\} \right]} \quad . \quad (50)$$

The effect of an inhibitor on the reaction velocity may be expressed by the equation :

$$v_0 = v(1 + p c/n_0) \quad . \quad . \quad . \quad (51)$$

where v , v_0 are the velocities with and without inhibitor. p is given for the two cases by :

$$p_{II} = \beta/\lambda \quad . \quad . \quad . \quad (52)$$

$$p_{III} = \beta n_0/\gamma n_1 \quad . \quad . \quad . \quad (53)$$

Equation (51) is identical with the empirical expression if p is a constant : this condition is clearly fulfilled by p_{II} but not by p_{III} , except (approximately) for small ranges of n_1 .

The use made by Jeu and Alyea¹ of data on the effect of inhibitors to estimate the polymer size requires further that the velocity should be directly proportional to the chain length. This has been tested for the constants employed in calculating the curves of Figs. 1 and 2 (Part II.) by comparing v_c/v_0 with v_c/v_0 for various values of N , with the following results, shown in Table I.

It is clear from the above that the relationship $\frac{v_c}{v_0} = \frac{v_c}{v_0}$ holds with sufficient accuracy when the uninhibited reaction is controlled by spontaneous deactivation, but is valid only for the early stages of a reaction

TABLE I.—EFFECT OF INHIBITOR ON VELOCITY AND CHAIN LENGTH.

N/n_0	v_0	v_c	v_0	v_c	v_c/v_0	v_c/v_0
Spontaneous Deactivation.						
1.0	100.0	50.0	102.0	51.0	0.50	0.50
0.7	48.7	23.9	85.8	43.8	0.49	0.51
0.5	24.3	12.0	73.7	37.6	0.49	0.51
0.2	3.5	1.5	50.6	25.8	0.43	0.51
Deactivation by Monomer.						
1.0	100.0	52.5	102.0	52.0	0.525	0.51
0.7	69.7	30.0	102.0	47.0	0.46	0.47
0.5	49.7	16.1	102.0	43.7	0.33	0.43
0.2	19.3	2.6	102.0	34.7	0.14	0.34

controlled normally by deactivation by monomer. This conclusion is of especial interest, since it has already been shown in Part II. that the photo-polymerisation of vinyl acetate studied by Jeu and Alyea¹ probably belongs to the latter class. Inspection of the results quoted by these workers shows that the experimental observations are very well represented by the equation valid for ordinary chain reactions, but there is a slight tendency for the observed values of the fraction polymerised (x) to be higher than the calculated ones at the highest inhibitor concentration (c). A plot of $1/x \sim c$, where x is measured always after the same time of reaction, thus tends to be concave towards the c -axis, whereas Jeu and Alyea's relationship gives a straight line. A relationship between x and c can be derived from the analysis given above, in the form :

$$\frac{1 + 2\gamma}{2 - x} + \frac{\beta c}{1 - x} - \frac{1}{(1 + 2\gamma)(2 - x) + 4\beta c} = \frac{k\gamma(1 + \gamma)}{x(1 + 2\gamma)} \quad (54)$$

where k is to be found from the rate of the uninhibited reaction. (A slight simplification has been made by putting

$$\ln 1/(1 - x) = 2x/(2 - x).$$

Taking $\gamma = 0.001$ (cf. Part II.) a plot of $1/x \sim c$ can be made by choosing β so as to fit a single experimental point. $\beta = 2.35$ was found to give a good fit of Jeu and Alyea's data for pyrogallol, and gave a ($1/x \sim c$) curve slightly concave towards the c -axis. The deviation from linearity is, however, too small to be significant over the range covered by the experiments ($x \geq 0.4$), although it would become a large correction if the range was extended to larger values of x . No decisive test of the theoretical treatment is therefore possible from existing data.

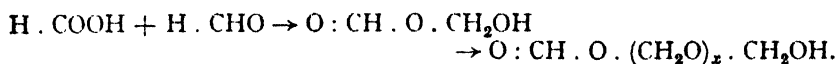
II. Catalysts.

We turn now to the consideration of catalysed polymerisation, and clearly the simplest possible mechanism is the initiation of chains by the catalyst, a case already considered by Dostal and Mark.⁴ The precise manner in which this catalysis occurs may vary in different reactions. Thus Conant and Peterson⁵ suppose that in the polymerisation of isoprene and butyraldehyde the first process is the formation of a peroxide which then dissociates to give an activated monomer which initiates a polymerisation chain. A similar mechanism has been proposed by Dunstan

⁴ Dostal and Mark, *Trans. Faraday Soc.*, 1930, **32**, 54.

⁵ Conant and Peterson, *J.A.C.S.*, 1930, **52**, 1659; 1932, **54**, 628.

and Ipatieff ⁶ for the catalytic effect of phosphoric acid on the polymerisation of propylene. Of a different type is the suggestion made by Norrish and Carruthers ⁷ as to the effect of formic acid in initiating polyoxymethylene chains, which is formulated thus :



A very simple formal treatment of this type of reaction can be given, as it is only necessary to add to the equations already given in Part II. the further one :



the rate of which is $\rho K c n_1$, where ρ is a constant and c is the number of molecules of catalyst. The first effect of this addition is to increase the polymerisation velocity by a factor

$$v = v_0(1 + \rho c / \alpha n_0) \quad . \quad . \quad . \quad . \quad . \quad (56)$$

The chain length is independent of the rate of chain initiation in Cases II. and III. (Part II.), but not in Cases I. and IV. In these mechanisms the chain length will be decreased by the catalyst, the magnitude of the effect being readily determinable by replacing α in equations (13) and (39) by α^* where

$$\alpha^* = \alpha + \rho \cdot \frac{c}{n_0} \quad . \quad . \quad . \quad . \quad . \quad (57)$$

For Case I. (no steric factor, no deactivation), we obtain, by combining (57) with (13),

$$\frac{v_c - 1}{v_0 - 1} = \sqrt{\frac{\alpha_0}{\alpha^*}} \quad . \quad . \quad . \quad . \quad . \quad (58)$$

This simple mechanism is inadequate to account for the complexity of the results observed, for in general the effect of catalysts on chain length may be in either direction. Thus styrene which by spontaneous polymerisation yields high polymers, may in the presence of catalysts be converted into distyrene.⁸ Dimethyl ketene, on the other hand, gives only a dimer spontaneously, but can be induced to give long chain products by addition of catalysts.⁹ The decrease of chain length is readily understood if the rate of chain initiation is a controlling factor, and could equally be brought about by the catalyst acting also as a chain breaking inhibitor. The explanation of increased chain length is by no means so clear, apart from a few cases where chain branching may be possible (*cf.* Norrish and Carruthers ⁷). It is suggested that the explanation of this phenomenon must be sought in the formation of unstable complexes between the catalyst and the polymerising material. The cumulative evidence for the existence of such complexes is strong, and it has been shown by Staudinger and Bruson ⁹ that the catalytic activity of the halides of some non-metals runs closely parallel with their tendency to form complexes. Thus BF_3 , SnCl_4 , and AlCl_3 , which are known to form complexes readily, are catalysts, while SiCl_4 and POCl_3 show neither catalytic activity nor tendency to form complexes. The suggestion that

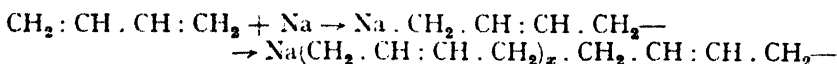
⁶ Dunstan and Ipatieff, *Trans. Faraday Soc.*, 1936, **32**, 227.

⁷ Norrish and Carruthers, *ibid.*, 1936, **32**, 195.

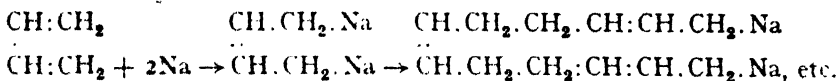
⁸ Stobbe and Posnjak, *Ann.*, 1910, **311**, 292.

⁹ Staudinger and Bruson, *ibid.*, 1926, **447**, 110.

complexes are formed as the initial stage of catalysed polymerisation has also been put forward by Abkin and Medvedev¹⁰ for the catalysis by sodium of the polymerisation of 1 : 3 butadiene, and by Chalmers¹¹ for the polymerisation of vinyl ethers in the presence of iodine. In the polymerisation of monolayers of oxidised drying oils there is also direct evidence from surface potential measurements that cobalt, which acts as a polymerisation catalyst, forms a complex with the film.¹² We have next to discuss the general mechanism by which the complex catalyses the polymerisation process, and two alternative suggestions have been put forward. Chalmers³ and Bergmann¹³ formulate the addition of catalyst to reactant in such a way that a free valency is produced. Thus the polymerisation of 1 : 3 butadiene by sodium would be written :



Abkin and Medvedev,¹⁰ on the other hand, formulate this reaction as



Neither of these proposals is quite satisfactory. In the former case, it is impossible to imagine the influence of the catalyst extending more than a few links, so that the active group is the same as in the uncatalysed reaction, and the mechanism reduces formally to the one already considered. On the other hand, the alternative explanation involves two apparent difficulties : (i) the necessity for migration of the catalyst to the active end of the polymer at every step in the reaction, and (ii) the reaction becomes virtually a "stepwise" reaction, which has been shown by Chalmers³ to be incapable of yielding long chain products. This dilemma may be avoided by the assumption of a mechanism similar to the well-known migration of atoms incident on the face of a growing crystal to the end of the crystal, where they take part in the building up process. It has been suggested by de Boer¹⁴ that this type of mechanism may be operative in the normal building up of polymers, and thus account for the very high rates of chain propagation. We may thus visualise the catalyst as remaining in association with the active portion of the growing polymer for a length of time which will vary with the natures of the reactant and catalyst. If the time is very short, we have virtually a collision mechanism, which reduces to the previous case ; a long time of association gives us complex formation in which the catalyst remains at the active and growing point. This latter case is examined in the next section.

IIa. Catalysis by Complex Formation.

We shall consider the catalysis of a chain in which termination normally occurs by collision with a monomer, and shall have in addition to the reactions represented by equations (3) and (30) the following processes :

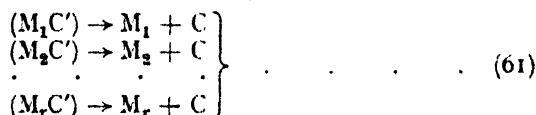
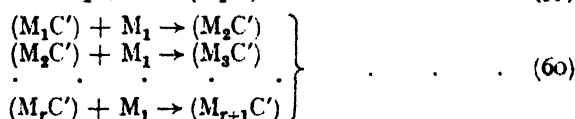
¹⁰ Abkin and Medvedev, *Trans. Faraday Soc.*, 1936, **32**, 286.

¹¹ Chalmers, *Can. J. Res.*, 1932, **7**, 476.

¹² Gee and Rideal, *Proc. Roy. Soc.* 1935, **153A**, 116; Gee, *ibid.* 1935, **153A**, 129; *Trans. Faraday Soc.*, 1936, **32**, 187.

¹³ Bergmann, *ibid.*, 1936, **32**, 295.

¹⁴ de Boer, *ibid.*, 1936, **32**, 69.



Equation (59) represents the formation of the initial complex, and its velocity constant is written as :

$$k^{IV} = K\alpha'c \quad . \quad . \quad . \quad . \quad (62)$$

Equations (60) give the building up of polymeric complexes, this process being terminated by dissociation of the complex, as in (61). The rates of these two processes are respectively

$$k_r^V = K \cdot \sigma \quad . \quad . \quad . \quad . \quad (63)$$

$$k_r^{VI} = K\lambda'n_0 \quad . \quad . \quad . \quad . \quad (64)$$

We have this time a further series of compounds (the complexes) whose concentrations are denoted by n'_{re} , and can be evaluated by writing down the appropriate stationary state equations. A further complication arises from the fact that the effective catalyst concentration depends on the amount of complex present and is therefore not constant. If c/n_0 , c_e/n_0 are the total and effective (uncombined) catalyst concentrations, then

$$c = c_e + \sum_{r=1}^{\infty} \frac{1}{r} n'_{re} \quad . \quad . \quad . \quad . \quad (65)$$

whence

$$c_e = \frac{\lambda'n_0c}{\lambda'n_0 + \alpha'n_1} \quad . \quad . \quad . \quad . \quad (66)$$

We may now proceed to derive the velocity equation in the usual way, and the result is :

$$-\frac{dN}{dt} = K \left[\frac{\alpha n_0 n_1}{\gamma} + \frac{\sigma \alpha' c n_1^2}{\lambda' n_0 + \alpha' n_1} \right] \quad . \quad . \quad . \quad (67)$$

The expression representing the variation of chain length is excessively complicated and only a formal solution will be given. By putting in numerical values of the constants ($1 - dN/dn_1$) can be obtained in the form :

$$1 - \frac{dN}{dn_1} = \frac{An_0^2 - Bn_0(n_0 - n_1) + D(n_0 - n_1)^2}{En_0^2 - Fn_0(n_0 - n_1) + (n_0 - n_1)^2} \quad . \quad (68)$$

where A , B , D , E and F are numerical constants.

Combining with equation (27) an expression is obtained which can be integrated to give a solution of the form :

$$v = \frac{a(n_0 - n_1)}{(n_0 - n_1) + bn_0 \log \left\{ \frac{dn_0}{(d-1)n_0 + n_1} \right\} + en_0 \log \left\{ \frac{fn_0}{(f-1)n_0 + n_1} \right\}} \quad (69)$$

where a, b, d, e and f are further numerical constants which are related to the former constants by the following equations :

$$\left. \begin{aligned} a &= 1/D \\ b) \\ e) &= 1.15 \left\{ (B/D - F) \pm \frac{BF - 2A}{D} + 2E - F^2 \right\} \\ d) \\ f) &= 0.5 (F \pm \sqrt{F^2 - 4E}) \end{aligned} \right\} \quad (70)$$

Catalysis by Complex formation

I $\alpha = 10^{-6}$; $\gamma = 10^{-2}$; $c = 0$

II $\alpha = 10^{-8}$; $\gamma = 10^{-2}$; $\frac{c}{n_0} = 10^{-2}$; $\sigma = 0.1$; $\lambda^1 = 10^{-3}$; $\alpha^1 = 0.1$.

III $\alpha = 10^{-6}$; $\gamma = 10^{-2}$; $\frac{c}{n_0} = 10^{-2}$; $\sigma = 1$; $\lambda^1 = 10^{-6}$; $\alpha^1 = 0.1$.

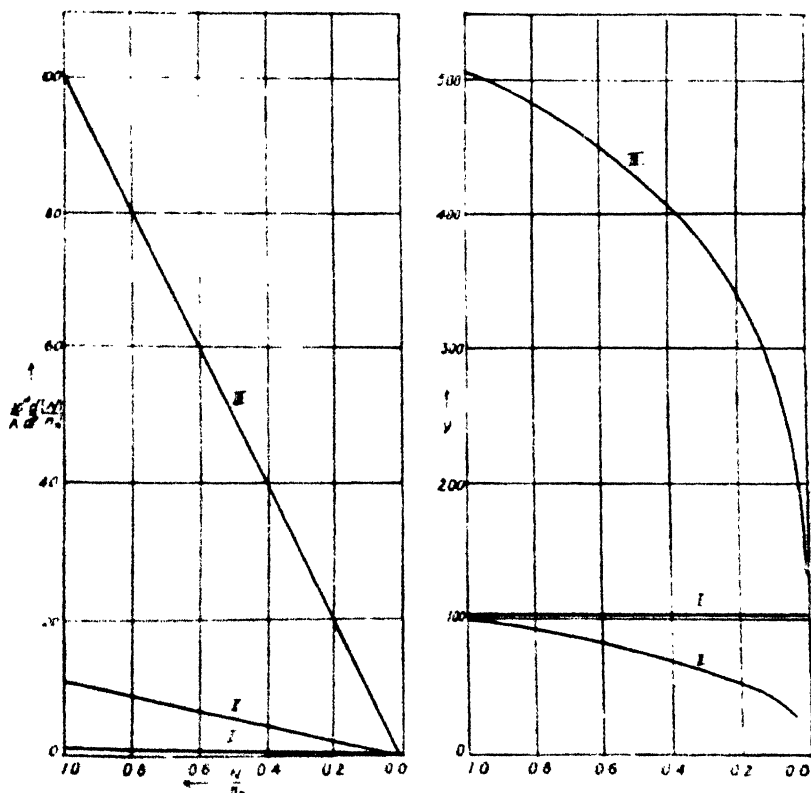


FIG. 5.

In Fig. 5 plots are given of $(dN/dt \sim N)$ and $(v \sim N)$ calculated for various values of the constants. It is evident from equation (67) that the catalytic effect must always be positive, but it is to be noted from the figure that this may be associated with either increase or decrease of the polymer size, so that this mechanism is able to include all the observed facts.

Summary.

The effect of an inhibitor on the velocity of a polymerisation reaction and the size of the polymers produced is examined, and it is shown that the usual assumption that these are diminished in the same ratio is not strictly accurate, but is a good approximation in the early stages of the reaction.

The mechanism of catalysis is discussed, and two possibilities are analysed in detail:

(i) The catalyst initiates chain centres.

(ii) The catalyst forms a reactive complex.

It is shown that the latter is capable of explaining all the experimental observations.

Thanks are due to the Imperial Chemical Industries (Dyestuffs Group) for a grant to one of us (G. G.) which rendered this work possible.

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THE PHOTOCHEMISTRY OF NITRITES, NITRATES, AND NITRO COMPOUNDS.

BY H. W. THOMPSON AND C. H. PURKIS.

Received 13th January, 1936.

Much attention has been paid in recent years to the photochemistry of molecules containing the chromophoric carbonyl group. With the exception of a few isolated measurements, particularly in reference to inorganic nitrates and nitrites, no corresponding studies have yet been reported for compounds containing the nitro or nitroso group, although the kinetics of the thermal decomposition of such compounds have been studied.¹ The spectrum and photochemical decomposition of nitrosyl chloride was examined by Kistiakowsky,² and the absorption spectra of nitroethane, ethyl nitrate and ethyl nitrite by Goodeve.³ Krishnan and Guha⁴ have recently made measurements on the absorption spectra of inorganic nitrates and nitrites, and Anderson, Crumpler and Hammick⁵ have discussed measurements on the photochemistry of two organic nitroso compounds.

It seemed desirable to make a systematic study of these compounds. The choice of substances amenable to investigation in the vapour state has obvious advantages, of which perhaps the most important is the greater chance of being able to analyse the absorption spectra and correlate them with the photochemical measurements. We have therefore chosen in the first place methyl and ethyl nitrates, methyl and ethyl nitrites, and nitromethane and nitroethane. Measurements on formaldoxime $\text{H}_2\text{C} = \text{N} \cdot \text{OH}$, and other oximes and their ethers, are in progress. The present paper deals with the absorption spectra of the first series of

¹ Steacie and others, *J. Chem. Physics*, 1934, **2**, 345; 1935, **3**, 344.

² *J.A.C.S.*, 1930, **52**, 102.

³ *Trans. Faraday Soc.*, 1934, **30**, 504.

⁴ *Proc. Ind. Acad. Sci.*, 1934, **1A**, 242.

⁵ *J.C.S.*, 1935, 1679.

compounds, in which an important difference is found from the results given by Goodeve.

Experimental Method.

Methyl nitrite was prepared by the method of Bertoni,⁶ by dropping amyl nitrite slowly on to methyl alcohol, heating the latter gently. The vapours given off were passed through a series of traps and water condensers and finally frozen out in a liquid air trap. The product was a greenish liquid. It was fractionated, and the middle fraction, which was completely volatile below 0° C., collected. The purity of this sample was tested by measurements of its vapour pressure and hence boiling-point. The data are given below. The extrapolated B. Pt. was -18° C., rather lower than the value given in International Critical Tables (-12° C.). Repetition with a fresh sample gave a similar result, from which it seems probable that the figure hitherto accepted is in error.

Ethyl nitrite was prepared by refluxing a commercial 15 per cent. solution in alcohol. The vapour was condensed in a trap of ice and salt, and then fractionated. Methyl nitrate was prepared by the method of Delépine,⁷ by the action of methyl alcohol on nitric acid. The product boiled at 66°-66.5° C., and this was in accordance with vapour pressure measurements.

Ethyl nitrate was obtained by fractionation of British Drug Houses product. Nitromethane was a commercial product purified by first drying with calcium chloride and then fractionating. Nitroethane was a Kahlbaum product repurified by fractional distillation.

The spectra were measured on a Hilger quartz spectrograph E 315, and the bands found were subsequently examined on a 3 metre concave grating with Eagle mounting, giving in the first order a dispersion of about 4 Å. per mm. Ilford Special Rapid or Panchromatic plates were used. The continuous source was a hydrogen discharge tube. The vapours were contained in glass absorption tubes of various lengths, with plane polished quartz ends cemented on. In some cases an all-quartz absorption cell, wired and heated electrically, was used.

For the measurements of the vapour pressures of the various substances the apparatus was similar to that described by Thompson and Linnett.⁸

Results.

(1) **The Vapour Pressures of Methyl Nitrate, Methyl Nitrite and Nitromethane.**—Goodeve⁹ determined the vapour pressure curves for ethyl nitrate, ethyl nitrite and nitroethane, but no data are given in the literature for the corresponding methyl derivatives.

The data are summarised in Fig. 1.

For **nitromethane** the extrapolated B. Pt. is 100.8° C. (*International Critical Tables*, 101° C.) and $\lambda = 8280$ Cals., giving the Trouton constant, λ/T_b , the Entropy Change at the boiling-point as 22.2. The results are represented by the equation,

$$\log_{10} p = -\frac{1800}{T} + 7.69.$$

With **methyl nitrate** the measured boiling-point is 66.5° C. (*Int. Crit. Tables*, 65°-66° C.) and $\lambda = 7800$ Cals., so that $\lambda/T_b = 23.0$. The vapour pressure equation is

$$\log_{10} p = -\frac{1694}{T} + 7.85.$$

⁶ *Gaz. Chim. Ital.*, 12, 438.

⁷ *Trans. Faraday Soc.*, 1935, 31, 1743.

⁸ *Bull. Soc. Chem.*, (3), 13, 1044.

⁹ *Ibid.*, 1934, 30, 501.

The measured B. Pt. for methyl nitrite is -18°C . (*Beilstein* -12°C .), $\lambda = 5000$ Cals. and $\lambda/T_0 = 19.75$. The equation for the vapour pressure is

$$\log_{10} p = -\frac{1098}{T} + 7.19.$$

It is evident that the degree of association of these compounds is not considerable.

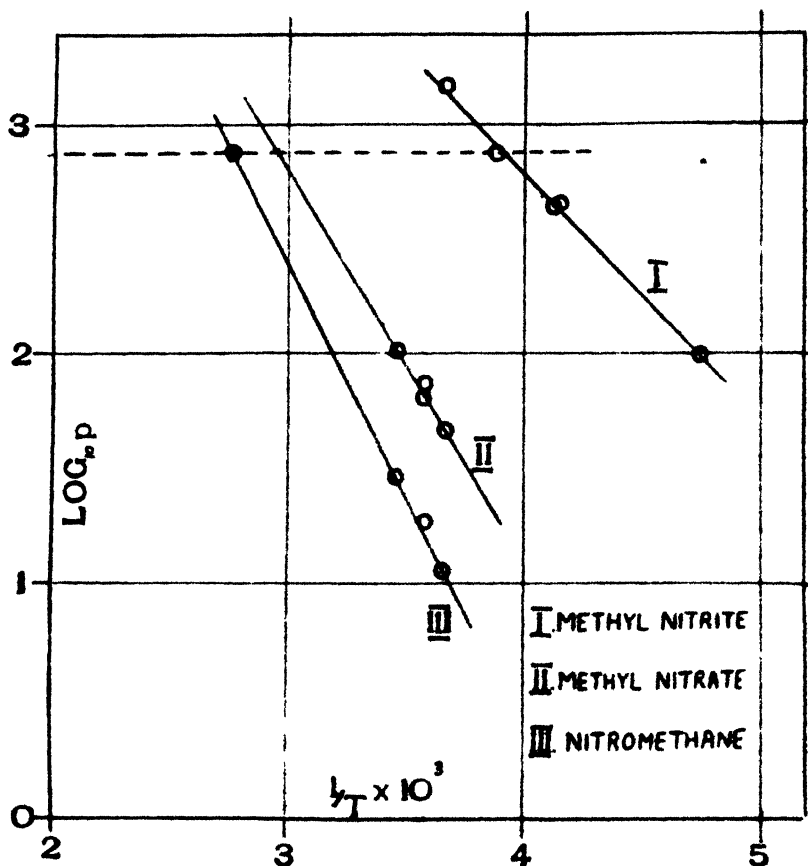


FIG. 1.

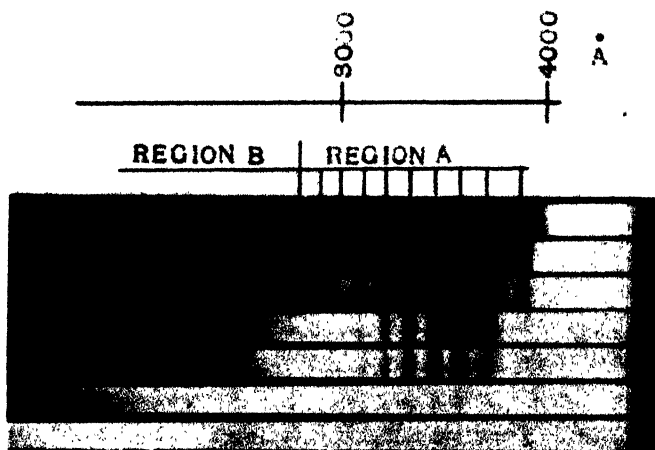
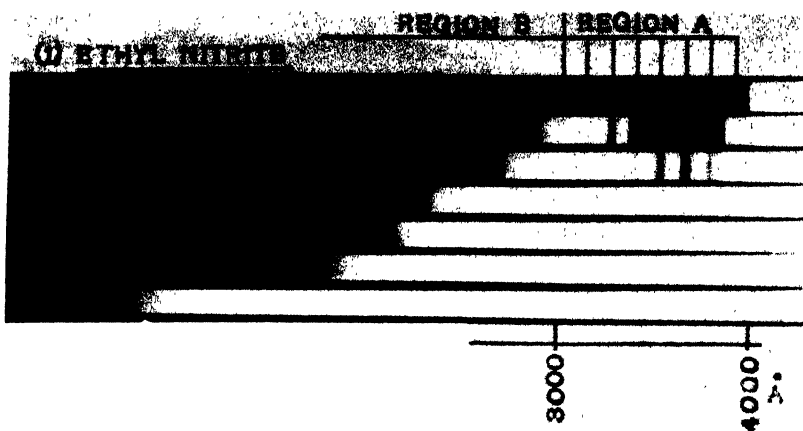
(2) The Absorption Spectra.

Methyl Nitrate.—With pressures of vapour 10-200 mm. in columns 10-50 cm. in length, absorption is continuous from a very indefinite long-wave limit at about 3000 Å. towards shorter wavelengths. The extinction coefficient does not vary uniformly with wavelength, the curve (not accurately measured) showing a point of inflexion at about 2500 Å.

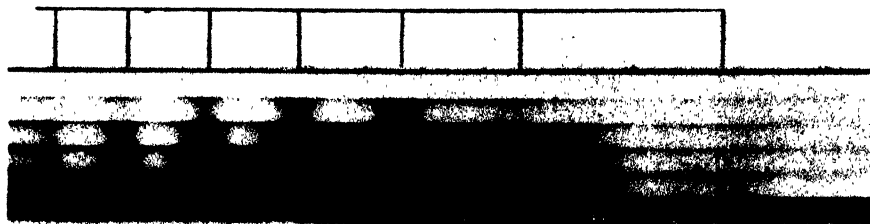
Ethyl Nitrate.—The spectrum is closely similar to that of methyl nitrate, the long-wave limit and variation of extinction coefficient with wavelength being within limits the same. This result agrees with that of Goodeve.

Nitromethane.—Continuous absorption is very marked from a fairly sharp limit at about 2350 Å. towards shorter wavelengths. A much feebler continuous absorption extended to about 2500 Å.

Nitroethane.—Absorption is continuous from about 3000 Å. to shorter



(2) METHYL NITRITE



(3) METHYL NITRITE (High dispersion)

wavelengths with a maximum at 2700 Å. and minimum at 2450 Å. This result agrees with that of Goodeve.

Ethyl and Methyl Nitrite.—According to Goodeve, ethyl nitrite shows continuous absorption to shorter wavelengths from a threshold at about 4000 Å., with a maximum at about 3640 Å. and a shallow minimum at 3030 Å. Absorption increases uniformly from the minimum to shorter wavelengths.

Our measurements with this substance agree completely with the above, except that at lower pressures we have resolved the first region of absorption between 4000-3000 Å. into a system of bands. In view of the strict agreement between ourselves and Goodeve for the long-wave threshold maximum and minimum, it seemed unlikely that the bands were due to some impurity or other error. The discovery, however, that with methyl nitrite

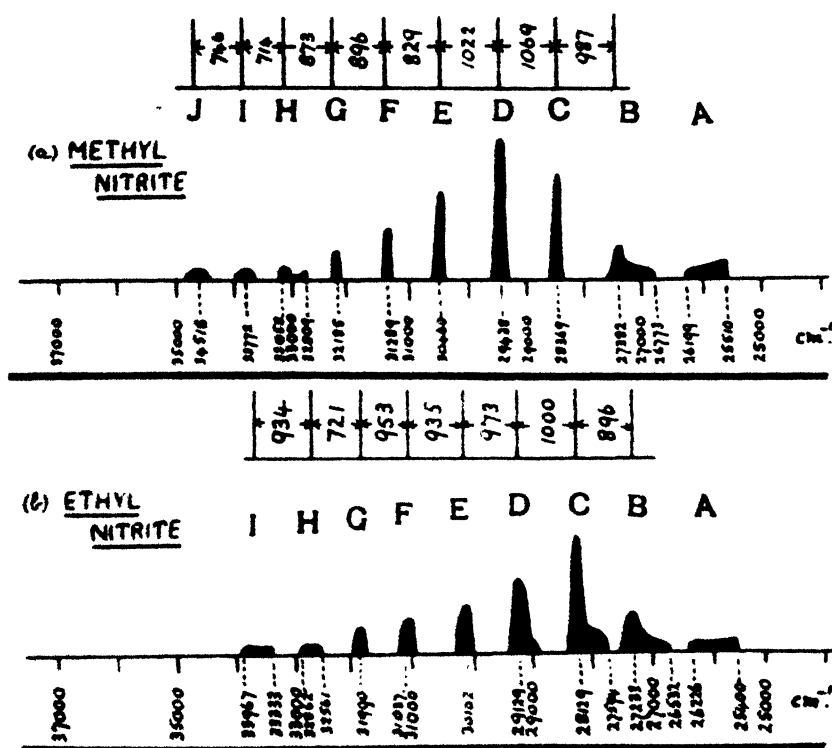


FIG. 2.

a similar system of bands is obtained, but differing slightly in wavelength from those of the ethyl compound, is adequate proof of their being genuine. With absorbing columns 10-20 cm. in length the most satisfactory pressure range for developing the bands is 10-50 mm. Goodeve's failure to detect the bands may have been due either to the nature of the method used (spectrophotometric), or to the use of too high pressures, when they become merged into a continuum.

The bands of methyl nitrite are shown in the plate, and depicted diagrammatically in Fig. 2a. They cannot be said to degrade with certainty in either direction, are broad, and although diffuse, show some features suggestive of fine structure. Examination under higher dispersion, however, failed to develop this. The breadth of the bands indicated by Fig. 2 is estimated roughly at the lowest pressures required for their development. The plate also shows the corresponding bands for ethyl nitrite, and their

wave numbers are given in Fig. 2*b*. The intensities shown in Figs. 2*a* and 2*b* are not accurate and are only intended as a qualitative guide.

Amyl Nitrite.—The results with methyl and ethyl nitrites suggest that in passing from the lower to the higher alkyl derivatives the band system is displaced to the red. The spectrum of repurified amyl nitrite was accordingly examined. It proved to be within the limits of the measurements identical with that of ethyl nitrite. The wide difference in vapour pressure between ethyl and amyl nitrite makes it inconceivable that the identical features of the two spectra arise from error.

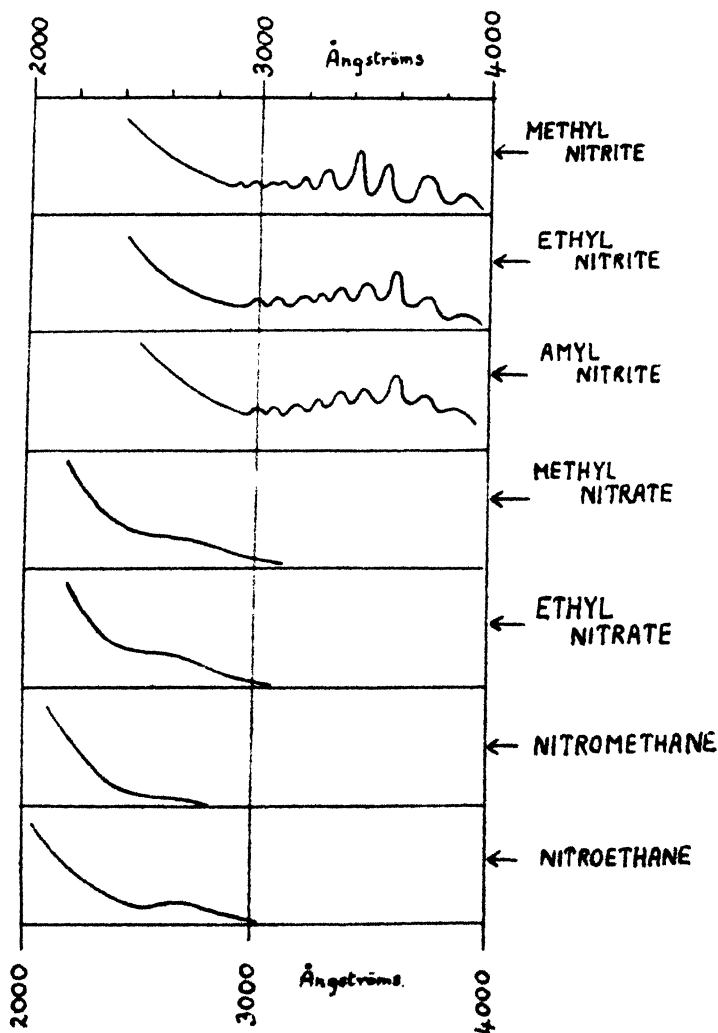


FIG. 3.

Discussion.

For purpose of comparison Fig. 3 shows the rough qualitative course of the extinction coefficients of the various compounds with varying wavelength.

It is clear that in the case of nitrites there are two excited electronic

levels, one associated with the bands, the other with the continuum. There may also be two excited state levels with the nitrates and nitro compounds, but if so these levels must lie closer together and further from the ground state.

It is important if possible first to determine the localisation of the electronic jump, which, in the case of any given compound, may or may not be the same for the two levels. By analogy with other compounds, such as ethers, it is unlikely that the electronic jump occurs in the alkyl radical or the R—O— of the nitrites, and it would thus appear to involve excitation of electrons localised in the region of the $N=O$ link. This result is also suggested from a comparison of the nitrites with the nitrates and nitro compounds. That the levels of the nitrites lie lower than those of the nitrates would not then be surprising, since two electrons of the nitrogen atom are not employed for valency purposes in the nitrites, and might be relatively easily excited.

The absence of a maximum in the continuum, and the marked effect of pressure upon the long wave-length limit, makes it impossible to assign a value to the quantum corresponding to this electronic transition. In the same way it has not so far been possible to determine the "origin" of the band systems of the nitrites; in passing from the methyl to the ethyl derivative, however, the electronic jump decreases somewhat in magnitude, but with higher homologues may reach a constant value.

The interval relationships between the bands suggest a vibration frequency in the excited state of about 1000 cm.^{-1} , with a high anharmonicity coefficient. The Raman spectra of alkyl nitrites are very complicated;¹⁰ it is also impossible to say whether the vibrational frequencies are increased or diminished in the excited state; it is therefore impossible to correlate the marked observed frequency of about 1100 with any particular normal vibration of the molecule. The magnitude of this frequency, however, is consistent with its being connected with a valency vibration of the $N=O$ link.

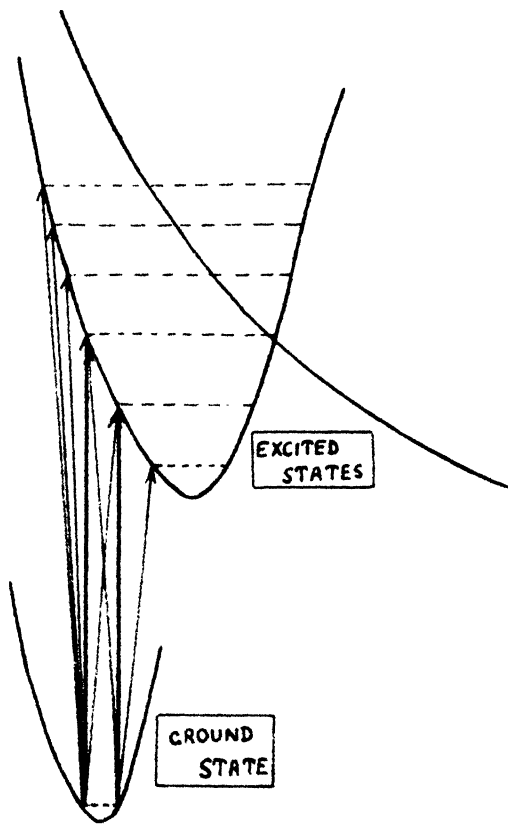


FIG. 4.

¹⁰ Dadiou, Jele and Kohlrausch, *Wien. Ber.*, 1931, 140.

The intensity distribution in the band systems, together with the Franck-Condon Principle, suggest the interpretation described by Fig. 4, but the significance of two-dimensional potential energy diagrams in this case is uncertain. The broad nature of the bands, A, B, H, I, and J with methyl nitrite, and of A, B, C, D, H, and I for ethyl nitrite, is peculiar, and requires further study. If the bands are genuinely diffuse, this may arise by a predissociation brought about by intersection of potential energy curves in the manner shown in Fig. 4. On the other hand, the variation of intensity within individual bands suggests some definite rotational structure.

Krishnan and Guha⁴ have suggested that in the case of inorganic nitrites the two excited levels are associated with the fission of an oxygen atom in two different states of excitation. The same hypothesis might apply to the two levels of the alkyl nitrites, but we do not regard this as likely. There is some similarity between the spectrum of nitrosyl chloride and the spectra of the alkyl nitrites. In the former case the electronic energy absorbed by the $N=O$ group eventually leads to a splitting of the $N-Cl$ link, although there is still some doubt whether the energy switch occurs in the primary act without the intervention of a collision with a second molecule. Similar switches of energy from a chromophoric group to other linkages in the molecule are now known, e.g. in the photochemical decomposition of aldehydes and ketones. It is probable that the electronic energy absorbed by alkyl nitrites first enters the $N=O$ group and is later distributed into the other linkages before dissociation occurs. The latter may follow a rather complicated course.

Photochemical measurements will be described later, when values of the quantum efficiency for the decomposition with frequencies corresponding to each of the two absorption regions will be compared.

Summary.

As a preliminary to photochemical work, the ultraviolet absorption spectra of methyl and ethyl nitrites, methyl and ethyl nitrates, and nitromethane and ethane in the vapour state have been measured. All except the nitrites show continuous absorption. The nitrites each have a system of diffuse bands in the near ultraviolet. The bands are not all of equal intensity, and some have a peculiar variation of intensity within themselves. A marked vibration interval in the excited state seems to be about 1000 cm^{-1} . There appear in general to be two excited electronic levels, both probably involving excitation of electrons localised in the $N=O$ chromophore. The significance of the results is discussed.

The vapour pressures of the various compounds over a wide range of temperature have been measured.

We thank the Government Grant Committee of the Royal Society for assistance in the purchase of apparatus.

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THE VAPOUR PRESSURES AND ASSOCIATION OF SOME METALLIC AND NON-METALLIC ALKYL.

BY H. W. THOMPSON AND J. W. LINNETT.

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In the course of a recent study of the absorption spectra of a series of metallic and non-metallic alkyls, it was necessary to know the vapour pressures of these compounds, over a wide range of temperature. Such data, especially with regard to the metal alkyls, are almost completely lacking. The present paper summarises measurements with some of these compounds. In a previous paper we have given the results for the alkyl sulphides.¹ Estimates were then made of the Trouton constant for the various substances since these are a possible guide to the degree of association in the liquid or gaseous phase. It is now possible to review the values of this quantity for the alkyl derivatives of elements of Groups II-VII. of the Periodic Table, and to make deductions concerning the extent of association of compounds of this type.

The vapour pressures of the following substances have now been measured: zinc dimethyl, zinc diethyl, mercury dimethyl, mercury diethyl, tin tetramethyl, triethyl phosphine, trimethylamine, triethylamine, and methyl iodide. Each was purified by the same method as described for the spectroscopic work.²

Experimental Method.

The vapour pressures were determined by using a Bourdon gauge as zero instrument against a mercury manometer. The arrangement of the apparatus is shown in the diagram. The substance was

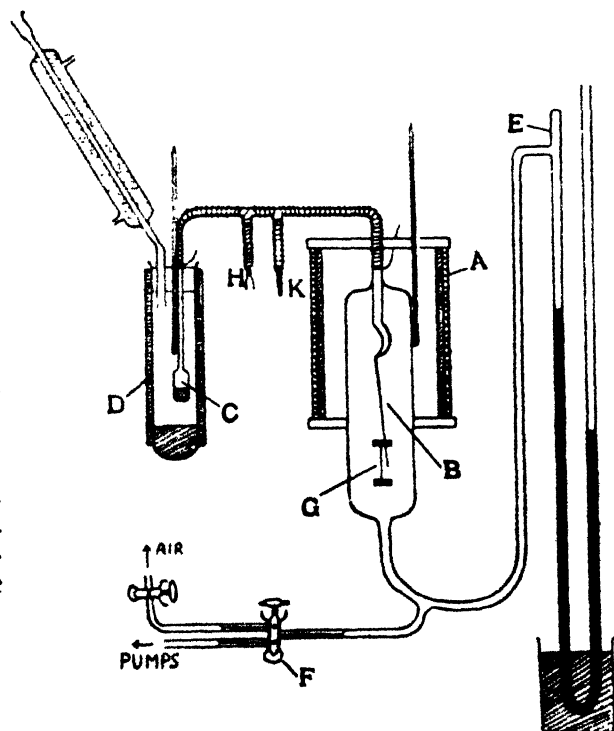


FIG. 1.

¹ *Trans. Faraday Soc.*, 1935, **31**, 1743.

² Thompson and Linnett, *Proc. Roy. Soc.*, 1936, *in the press*.

enclosed in a glass bulb C, connected to the gauge B, which had a fine solid pointer, the tip of which was coated with white enamel. Pressures inside the gauge were balanced by regulation of the mercury manometer E, (11 mm. bore), through the tap at F, which could be opened either to an oil pump or to the atmosphere. A fine glass capillary G was fixed to the back of the cylindrical glass tube holding the gauge. This was the "zero" mark, superposition with the pointer being observed through a small microscope. The apparatus was wired and heated electrically to about 90° C., and the upper part of the gauge was enclosed in an electric furnace maintained at a constant temperature of about 90° C. The bulb C could be enclosed in a wide glass tube D, suitably lagged, in which liquids of different boiling-point could be refluxed. The temperature of the vapour was measured by a standard thermometer. The levels of E were read off on a cathetometer. In general the liquid to be studied was distilled into C from a tube attached at H, the latter then being sealed off by a constriction. A little of the substance was then pumped off at K, C was surrounded by liquid air, and the apparatus evacuated and sealed off at K. The difference in the levels of E when C was immersed in liquid air was taken as the barometric height.

Liquids used in the refluxing chamber D were acetone, chloroform, ethyl ether, benzene, methyl alcohol, etc., all boiling below about 80° C. Cooling baths of melting ice, melting benzene, or melting aniline were also used.

Results.

(1) **Zinc Dimethyl.**—The measured vapour pressures at different temperatures were :—

$t^{\circ}\text{C.}$	— 6.2	0	5.5	16.6
p mm.	91	125	154	248

The plot of $\log_{10} p$ against $1/T$ is a good straight line, which on extrapolation to 760 mm. gives a B.Pt. of 46.9° C. (*Int. Crit. Tab.* 46° C.). The line can be expressed by

$$\log_{10} p = -\frac{1486}{T} + 7.52.$$

The latent heat of evaporation, λ , is thus 6840 Cals. per Mol., and λ/T_b , the Trouton constant or Entropy Change at the B.Pt., has the value 21.4.

(2) **Mercury Dimethyl.**—The measured vapour pressures are :—

$t^{\circ}\text{C.}$	20.5	36.0	55.3	59.8	63.7	78.7
p mm.	50	103	217	255	297	477

The plot of $\log_{10} p$ against $1/T$ is a satisfactory straight line, but at low temperatures there are indications of a slight curvature. The extrapolated B.Pt. is 93.2° C. (recorded value 93°-96° C.). The line can be expressed by

$$\log_{10} p = -\frac{1720}{T} + 7.575$$

the latent heat $\lambda = 7910$ Cals., and $\lambda/T_b = 21.6$.

(3) **Zinc Diethyl.**—The measured values are :—

$t^{\circ}\text{C.}$	17.2	35.0	55.3	60.4	64.8	79.8
p mm.	13	32.5	73.0	90.0	108	196

The plot of $\log_{10} p$ against $1/T$ is a fairly good straight line, expressed by

$$\log_{10} p = -\frac{1910}{T} + 7.695$$

and giving an extrapolated B.Pt. 123° C. (recorded value 118° C.). Then $\lambda = 8780$ Cals. and $\lambda/T_b = 22.2$.

(4) **Mercury Diethyl.**—The high boiling-point of this substance made it impossible to measure pressures in excess of about 50 mm. At 64° C., $p = 28$ mm., and at 80° C. $p = 54$ mm. The recorded B.Pt. is 159° C. For these points the plot of $\log_{10} p$ against $1/T$ is linear, and represented by

$$\log_{10} p = -\frac{2200}{T} + 7.975$$

and $\lambda_{10,120}$ Cals. Then $\lambda/T_b = 23.4$.

(5) **Tin Tetramethyl.**—The vapour pressures are :—

t° C.	18	35.5	55.8	59.5	64.0	78.9
p mm.	87.5	172	376	425	492	787

With the exception of the value at the lowest temperature the plot of $\log_{10} p$ against $1/T$ is linear, and expressed by

$$\log_{10} p = -\frac{1620}{T} + 7.495.$$

The extrapolated B.Pt. is 77.7° C. (recorded value 76°–78° C.); $\lambda = 7450$ Cals. and $\lambda/T_b = 21.2$.

(6) **Trimethylamine.**—The data are :—

t° C.	— 6.2	0	5.0	11.0
p mm.	516	680	804	1018

The plot of $\log_{10} p$ against $1/T$ is roughly linear, giving a B.Pt. of 3.2° C., (*Beilstein* 3.2°–3.8° C.), and

$$\log_{10} p = -\frac{1265}{T} + 7.45,$$

giving $\lambda = 5820$ Cals. and $\lambda/T_b = 21.1$.

(7) **Triethylamine.**—The vapour pressures are :—

t° C.	12.4	35.0	56.6	60.5	64.4
p mm.	38	106	247	282	328

The plot $\log_{10} p$ against $1/T$ is a good straight line, expressed by

$$\log_{10} p = -\frac{1725}{T} + 7.625$$

and giving $\lambda = 7930$ Cals. The extrapolated B.Pt. is 90.3° C. (*Int. Crit. Tables*, 89.5° C.). The value of $\lambda/T_b = 21.9$.

(8) **Triethyl Phosphine.**—The vapour pressures were :—

t° C.	18	36	55.1	59.3	63.5	78.2
p mm.	10	24	56	70	79	143

There is good proportionality between $\log_{10} p$ and $1/T$, expressed by,

$$\log_{10} p = -\frac{2000}{T} + 7.86.$$

The extrapolated B.Pt. is 128.6° C. (*Int. Crit. Tables*, 128° C.) $\lambda = 9200$ Cals., and $\lambda/T_b = 22.8$.

(9) **Methyl Iodide.**—The present measurements give :—

t° C.	0.1	4.3	11.7	34.4
p mm.	142	171	235	569

These data are satisfactorily represented by the equation,

$$\log_{10} p = -\frac{1475}{T} + 7.56,$$

in excellent agreement with the measurements of Brown and Acree,^a

^a *J.A.C.S.*, 1916, 38, 2145.

and of Robertson and Acree.⁴ The extrapolated B.Pt. is 42.8° C. (recorded 43° C.), $\lambda = 6790$ Cals. and $\lambda/T_b = 21.5$.

Discussion.

It may now be profitable to consider the values of the Trouton constant for the alkyl derivatives of elements of different groups of the Periodic Table. These are set out below.

GROUP IN THE PERIODIC SYSTEM.

I.	II.	III.	IV.	V.	VI.	VII.
[Li(C ₂ H ₅) ₃]		B(CH ₃) ₃ , 21.6			O(CH ₃) ₂ , 22.3	FCH ₃ , 21.0
[Na(CH ₃) ₃]	Zn(CH ₃) ₂ , 21.4	[Al(C ₂ H ₅) ₃]		N(CH ₃) ₃ , 21.1	O(C ₂ H ₅) ₂ , 20.2	ClCH ₃ , 21.2
	Zn(C ₂ H ₅) ₂ , 22.2	[Al(C ₂ H ₅) ₃]		N(C ₂ H ₅) ₃ , 21.9		BiC ₂ H ₅ , 21.4
	Hg(Cu) ₂ , 21.6	[Ga(CH ₃) ₃]	Ge(C ₂ H ₅) ₄	P(C ₂ H ₅) ₃ , 22.8	Si(CH ₃) ₂ , 22.3	ICH ₃ , 21.5
[Na(C ₂ H ₅) ₃]	Hg(C ₂ H ₅) ₂ , 23.4	[Ga(CH ₃) ₃]	Sn(CH ₃) ₄		Si(C ₂ H ₅) ₂ , 21.7	ClC ₂ H ₅ , 22.1
		[In(CH ₃) ₃]	21.2			IC ₂ H ₅ , 21.7
		[Tl(C ₂ H ₅) ₃]				

The value given for boron trimethyl is calculated from the vapour pressure data of Stock,⁵ and those for the alkyl halides from the vapour pressure data given in *International Critical Tables*. Values for the ethers and thioethers have previously been given.¹ The physical properties of the alkali metal alkyls indicate association in the solid state; and cryoscopic measurements with lithium ethyl are said to indicate six-fold association. According to Louise and Roux,⁶ aluminium triethyl and aluminium tripropyl are associated in the vapour state. The Trouton constant for gallium triethyl evaluated from the vapour pressure measurements of Dennis and Patnode⁷ is 23.9, suggesting slight association, in the liquid phase. From cryoscopic data these observers suggest association to double molecules. The Trouton constant of gallium trimethyl is 23.9 too,⁸ which may similarly imply slight association. Indium trimethyl is a solid, which from cryoscopic data of Dennis⁹ appears to be associated four-fold. The extent of association of thallium triethyl has not been estimated, but since this substance is a liquid of very high B.Pt., it may well be abnormal. From the vapour density and from cryoscopic data, Dennis¹⁰ has concluded that germanium tetra ethyl is unassociated.

None of the other substances examined in the present work and listed above show a noticeable divergence from the "normal" value of the constant, about 21.7, and suggesting that none are appreciably associated. The rather high value for mercury diethyl is suggestive of slight association, but in this particular case the errors are most noticeable, and the result may be accidental.

Thus in so far as the table is representative and complete, the only compounds showing association are the alkyl derivatives of the elements of Group I. (alkali metals) and of the heavier elements of Group III.

⁴ *Am. Chem. J.*, 1913, 49, 474.

⁵ *Ber.*, 1921, 54, 531.

⁶ *Comptes Rendus*, 1888, 107, 601; *Bull. Soc. Chim.*, 1888, (2), 50, 511.

⁷ *J.A.C.S.*, 1932, 54, 182.

⁸ Kraus, *Proc. Nat. Acad. Sci.*, 1933, 19, 292.

⁹ *J.A.C.S.*, 1934, 56, 1047.

¹⁰ *Ibid.*, 1925, 47, 370.

An explanation of this peculiarity on the basis of the electronic theory of valency cannot at present be suggested. The physical properties of the beryllium and magnesium alkyls suggest, however, that these compounds may be associated, so that the conclusions may not be as simple as just stated.

Summary.

The vapour pressures of a series of metallic and non-metallic alkyls have been measured over a range of temperature. The Trouton constants thus calculated indicate that these compounds show little, if any, association. The degree of association of other similar substances is discussed.

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THE CRITICAL SOLUTION TEMPERATURES OF SOME ALIPHATIC ACIDS WITH NITROMETHANE.

BY G. BROUGHTON AND D. C. JONES.

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Few determinations have been made of the solubility relations of the higher fatty acids, particularly in solvents with which they are only partially miscible. A number of binary systems, containing a low aliphatic acid as one component,* have, however, been fully investigated, and the usefulness of the critical solution temperature of the system as a criterion of their purity demonstrated. In the present work the solubility curves of a number of the higher acids with nitromethane have been obtained. Nitromethane was chosen as the second component because it gives critical solution temperatures over a convenient temperature range with all the acids from caproic to stearic and is easily obtained pure. The use of a single liquid for second component also permits the relation between solubility and increasing chain length to become apparent.

Since there are few methods of estimating the purity of the higher fatty acids and their freedom from homologues, the effect of adding a third acid upon their critical solution temperature was also investigated.

Experimental.

Purification of Materials.—The acids were the same as those used in a previous paper,⁴ in which their preparation and physical constants are given.

Nitromethane was prepared from sodium monochloracetate by treatment with sodium nitrite.¹ After treating with ice-cold 85 per cent. sulphuric acid and washing with saturated sodium sulphate solution, it was

* *E.g.*, formic acid-benzene,¹ acetic acid-carbon disulphide,² acetic acid-cyclohexane,³ butyric acid-water.³

¹ Timmermans and Hennault Roland, *J. Chim. Physique*, 1930, 27, 401.

² Jones, *J.C.S.*, 1923, 123, 1374.

³ Rothmund, *Z. physik. Chem.*, 1898, 26, 433.

⁴ Broughton, *Trans. Faraday Soc.*, 1934, 30, 367.

⁵ *Organic Syntheses* III, 83.

TABLE I.

Percentage Acid (by Weight).	Miscibility Temp.	Percentage Acid.	Miscibility Temp.
Caproic Acid—Nitromethane.			
22.74	— 7.20° C.	46.96	— 3.50
25.02	— 6.20	50.58	— 3.65
25.36	— 5.85	50.79	— 3.65
33.75	— 3.85	52.60	— 3.80
36.83	— 3.55	55.40	— 4.20
38.95	— 3.45	59.29	— 5.25
41.35	— 3.40	66.00	— 8.05
43.96	— 3.40	67.11	— 8.90
Caprylic Acid—Nitromethane.			
13.15	22.00	42.37	34.85
19.00	29.10	44.32	34.72
24.04	32.55	48.61	34.64
30.89	34.30	54.29	34.05
35.28	34.80	60.78	32.15
40.47	34.85	69.11	27.55
Pelargonic Acid—Nitromethane.			
19.71	43.80	42.10	48.55
24.21	46.30	47.41	48.55
29.96	48.05	54.83	47.60
35.14	48.50	59.36	46.55
41.10	48.55	69.28	40.85
Lauric Acid—Nitromethane.			
13.48	69.10	40.72	78.90
20.18	75.20	42.10	78.80
26.01	77.65	50.44	78.60
33.29	78.70	58.12	76.95
39.34	78.80	68.23	71.85
Palmitic Acid—Nitromethane.			
12.14	94.05	37.48	104.55
18.45	101.60	38.95	104.50
22.90	102.75	45.77	104.45
28.44	103.95	53.15	103.55
31.97	104.15	58.93	101.65
33.36	104.30	61.80	100.50
34.30	104.30	72.84	92.40
Stearic Acid—Nitromethane.			
37.555	114.0	40.61	114.0
		43.33	114.0

TABLE II.

Acid.	Critical Solution Temperature.
Capronic . . .	— 3.40° ± 0.05° C.
Caprylic . . .	34.85
Pelargonic . . .	48.60
Lauric . . .	78.90
Palmitic . . .	104.55
Stearic . . .	114.0 ± 0.1° C.

fractionated. The fraction used had an ethereal odor, n_D^{25} 1.3796; d_4^{25} 1.1308.

Determination of the Solubility Curves.—The synthetic method, as described by Jones and Betts,^a was used with the substitution of mechanical shaking. Liquids were introduced into the glass tubes by pipettes, solids by a small glass funnel, the tip of which reached to the bottom of the tubes. Care was taken to ensure that all apparatus was dry. The temperatures at which complete miscibility occurred were taken to 0.05° C. by thermometers carefully standardised against a set of standard thermometers having N.P.L. certificates. The miscibility temperatures were very sharp especially for the lower acids and critical phenomena were also marked.

The results are shown in Tables I. and II., and Fig. 1 illustrates a typical solubility curve.

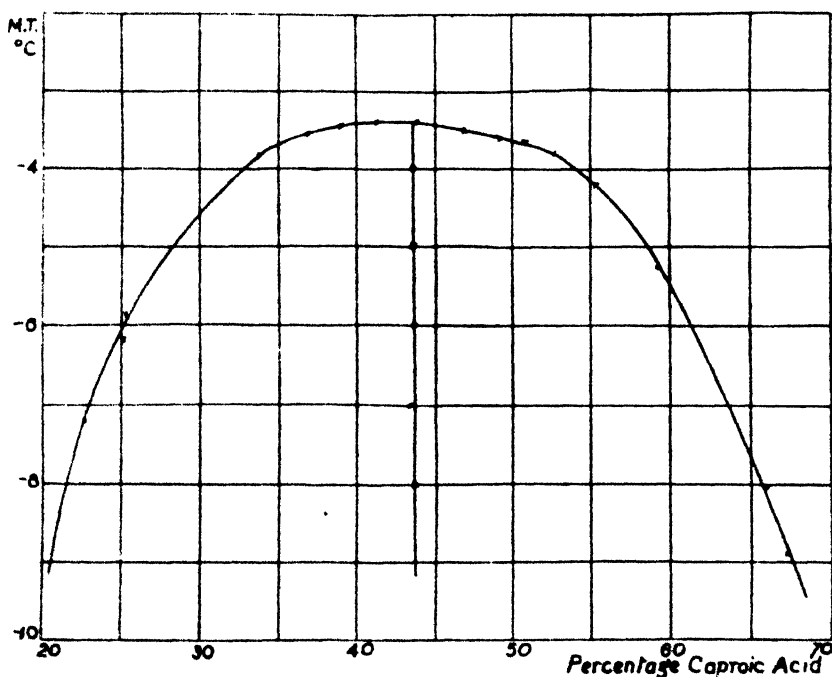


FIG. 1.

Effect of Homologues Upon the Critical Solution Temperature.

The effect of adding a third acid upon the consolute temperatures of caproic and palmitic acids was also roughly investigated. Mixtures containing 1-5 per cent. of another fatty acid were made up by direct weighing, and a few points in the neighbourhood of the critical solution temperature determined, using the mixture in place of the pure acid. The results are shown in Table III.

TABLE III.

System.	Added Impurity.	Percentage Required to Raise or Lower C.S.T. 0.1° C.
Caproic acid—Nitromethane	Butyric acid	0.16
" " "	iso-Butylacetic acid	0.51
" " "	Caprylic acid	0.29
Palmitic acid—Nitromethane	Stearic acid	1.17
" " "	Oleic acid	1.06

^a Jones and Betts, *J.C.S.*, 1928, 1177.

Discussion.

It will be seen that the solubility curves take the usual form, but with the exception of caproic and pelargonic acids the mean concentration lines curve within about 1° of the critical solution temperature. A possible explanation of this is that the acids used may still have been slightly impure.⁶

The solubility of the acids is seen to decrease in a regular manner with their position in the homologous series. In Fig. 2 the critical solution temperatures are plotted against the number of carbon atoms in the acid giving a perfectly smooth curve, from which the critical solution temperatures of acids not investigated can be predicted with an accuracy of at least 1° . In the same figure are shown data for aniline-hydrocarbon systems⁷ which give a similar smooth curve, showing, however, a minimum at hexane. The diminishing rise in critical solution

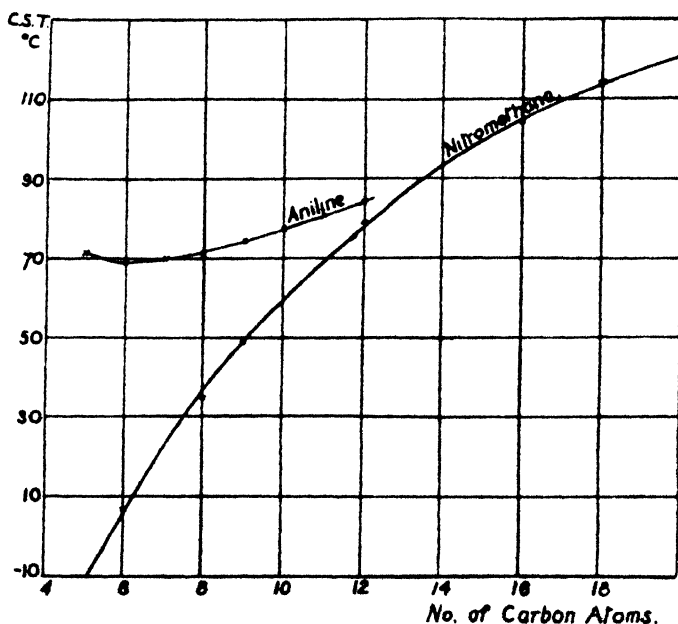


FIG. 2.

temperature with each addition of a $-\text{CH}_2$ -group would be expected, since the influence of the carboxyl group, at first predominant, becomes smaller with each addition, the molecule finally behaving almost as a hydrocarbon. The effect of the aliphatic hydrocarbons on the critical solution temperature with nitromethane has been determined already by H. J. Moss in this laboratory. A linear relationship was found, the slope being almost the same as that obtained in this work with the higher aliphatic acids. These two sets of results afford a good opportunity of testing the Langmuir theory of independent surface action,⁸ and this will be done in a further communication.

It is apparent from Table III. that the critical solution temperatures of the aliphatic acids cannot be used as sensitive criteria of their purity.

⁷ Shepard, Henne, and Midgley, *J. Am. Chem. Soc.*, 1931, **53**, 1948.

⁸ *Colloid Symposium Monograph*, **3**, 1925, 48.

Even in the case of caproic acid the effect produced by impurity is small, and in most cases the setting point is a more sensitive test.

Summary.

The critical solution temperatures of caproic, caprylic, pelargonic, lauric, palmitic and stearic acids with nitromethane have been determined and found to increase regularly with increasing molecular weight of the acid. The effect of homologues upon the critical solution temperatures has also been investigated.

During the period when this work was done one of the authors (G. B.) held a studentship of the University of London, and also obtained a research grant from the Chemical Society which defrayed, in part, the cost of the materials.

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THE INFLUENCE OF PHYSICAL STATE ON THE ABSORPTION AND FLUORESCENCE SPECTRA OF ORGANIC SUBSTANCES.

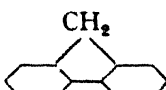


BY P. K. SESHAN, *Research Scholar, Indian Association for the Cultivation of Science, Calcutta.*

Received 7th January, 1936.

1. Introduction.

In the course of our investigations on the absorption and fluorescence spectra of aromatic compounds, we had occasion to study some of them in different physical states: vapour, liquid, solid, solutions in different solvents, and also solid solutions. The results are reported in the present paper. The spectra in the different states are compared with those in the vapour state, and the influence of the proximity of the surrounding molecules (*a*) of the same kind as the absorbing or the fluorescing molecule, as in liquid or solid, (*b*) of different kind, as in solutions, on the absorption and fluorescence spectra, is discussed.

2. Absorption Spectra.

The three aromatic hydrocarbons, fluorene  naphthalene , and perylene  were chosen for these investigations, since their absorption bands are sharp and well-defined, and attention was confined to the first few bands, which are very prominent.

The experimental arrangements adopted in these measurements were the same as those described in an earlier publication ¹ by the author, to

¹ *Proc. Ind. Acad. Sci.*, 1936, 3.

which the reader may be referred for the details. We shall content ourselves with giving the final results.

In Table I. are given the absorption data for fluorene under different physical conditions.² The positions of the absorption maxima are given in wave-numbers, and in the next column of the table are given the differences in wave-numbers between successive absorption bands.

Table II. gives similarly the absorption data for naphthacene and perylene. These two substances were studied in great detail in solutions. Two sets of investigations were made. In the first set the solvent was kept the same, and the absorption spectrum of the solute was studied for different concentrations. Owing to the low solubility of both these

TABLE I.—ABSORPTION SPECTRUM OF FLUORENE.

Vapour.		Alcoholic Solution.		Molten Liquid.		Solid Solution in Diphenyl.		Solid.	
ν .	$\Delta\nu$.	ν .	$\Delta\nu$.	ν .	$\Delta\nu$.	ν .	$\Delta\nu$.	ν .	$\Delta\nu$.
27200		26770		26320		26000		26000	
	410		400		400		410		410
27610		27170		26720		26410		26410	
	1030		990		1030		1010		1010
28640		28160		27750		27420		27420	
	420		360		350		390		390
29060		28520		28100		27810		27810	
	1050		1100		1100		1120		1120
30110		29620		29200		28930		28930	
	410		400				390		390
30520		30020		1450		29320		29320	
	1010		1170				1160		1160
31530		31190		30650		30480		30480	
	410		300				330		330
31940		31490				30810		30810	
	1060		1070				1030		1030
33000		32560				31840		31840	

TABLE II.—ABSORPTION SPECTRA OF NAPHTHACENE AND PERYLENE.

State.	Refractive Index.	Naphthacene.		Perylene.	
Vapour		22220	23630	24030	25500
Soln. in ether	1.354	21450	22900		
acetone	1.359	21410	22820		
alcohol	1.362	21340	22800	22980	24440
chloroform	1.446	21230	22670		
CCl ₄	1.465	21220	22660	22800	24260
m-xylene	1.499	21200	22640		
benzene	1.501	21200	22640	22770	24230
nitrobenzene	1.552	21160	22570		
CS ₂	1.629	20700	22170	22110	23580
Solid soln. in anthracene		20610	22070		
chrysene		20610	22070		

² As we mentioned in an earlier paragraph, we are giving here the positions of only the first few prominent bands in the absorption. For the complete absorption spectrum of this substance, as also of naphthacene and perylene, see *Proc. Ind. Acad. Sci.*¹

substances, all the concentrations studied were small. *For these dilute solutions, the positions of the absorption bands were found to be practically independent of the concentration.*

In the second set, the absorption spectrum of the substance was studied in different solvents, and the positions of the bands were found to vary, as will be seen from the table, from solvent to solvent. This variation will be clear from Figs. 1 and 2, in which are exhibited the absorption spectra of naphthacene and perylene respectively, in three typical solvents (alcohol, benzene, and carbon bisulphide), taken in juxtaposition with the help of a Hartmann diaphragm placed in front of the spectrograph (Hilger Quartz E_2).

3. Discussion of Results.

On comparing the absorption spectra of a substance in the different physical states, we observe, as we pass from vapour to the solutions and thence to the liquid and solid states, (1) a progressive broadening of the absorption bands, and (2) a progressive shift of the band system as a whole towards the red, the relative dispositions of the components of the band system remaining practically unaltered.

Since the *relative* positions of the component bands are determined by the vibrational frequencies of the molecule, in the normal and in the excited states, while the position of the band system as a whole depends on its electronic frequency, result (2) indicates that the vibrational frequencies of a molecule remain practically the same in the different physical states, whereas its electronic frequency diminishes progressively as we pass from the vapour to more and more dense states.

The actual magnitude of the shift of the bands towards the red as we pass from the vapour to the different physical states is given in the following table :—

TABLE III.—DISPLACEMENTS OF THE BANDS WITH REFERENCE TO THEIR POSITIONS IN THE VAPOUR STATE.

Substance.	Solution in C_2H_5OH CS_2 .		Liquid.	Solid.
Anthracene	880		—	2000
Naphthacene	850	1520	—	1580
Perylene	1050	1920	—	—
Phenanthrene	880		—	1440
Fluorene	430		880	1200

A comparative study of the positions of the bands for the solutions in the different solvents throws some light on the factors that influence the shift of the bands. In Table II. the solvents are arranged in the order of the increasing shift of the absorption bands, and on careful examination we find that this is also the order of increasing refractive index of the solvent, and of the solutions also, since the concentrations are small; *i.e., the greater the refractive index of the medium in which the absorbing molecules are dispersed, the greater is the shift, towards the red, of the absorption bands of the molecules, from their positions in the vapour state.*

An examination of the shifts in other physical states shows that the above result is very general, and holds not only for the solutions in

different solvents, but also for other physical states in which the absorbing molecules may be present, *i.e.* the result holds whether the molecules in the medium surrounding the absorbing molecules are of the same kind as the absorbing molecules or are of a different kind. For example, the molten liquid has a higher refractive index than the solutions, and the solid higher than the liquid. The shifts of the absorption bands from their positions for the vapour state follow also the same order, *vis.*, solutions, liquid, solid.

If this conclusion is correct, since the refractive index of a solution changes with its concentration, we should expect the absorption bands to shift as the concentration increases. For the low concentrations studied by us, the change in the refractive index should be too small to give an appreciable shift of the bands; the apparent independence of the positions of the bands in these dilute solutions, on the concentration, should doubtless be attributed to this circumstance. With suitable solutions, however, whose refractive indices can be varied considerably by changing the concentration, *e.g.*, phenanthrene in ether, the absorption bands of the concentrated solution are found experimentally to be slightly displaced towards the red, with reference to the corresponding bands of the dilute solution.

It should be remarked here that, in the solutions that we are considering, the solute molecules, *vis.*, naphthacene, perylene, phenanthrene and fluorene, are presumably all non-polar, *i.e.*, have no permanent electric dipole moment. When, on the other hand, the solute molecules are polar, it is quite possible that the polarity of the solvent molecules may also have an influence on the absorption spectra, and the refractive index of the medium may not be the main factor influencing the absorption, as is the case with non-polar solutes.

4. Influence of the Refractivity of the Medium on the Positions of the Absorption Bands.

The influence of the refractivity of the medium in shifting the absorption bands may be explained in the following manner. In the usual Lorentz treatment of the refractivities of dense media, it is shown that the actual electric field (of the light-vector) acting on any given molecule in the medium, is greater than the "field in the medium" by a factor θ given by the relation

$$\theta = 1 + 4\pi\chi/3 = (n^2 + 2)/3,$$

where χ is the polarisation of the medium per unit volume per unit field, and n is its refractive index. The consequence is an apparent increase in the refractivity of the densely packed molecules as compared with that of the molecules in the gaseous state.

This increase of refractivity due to close-packing may also be viewed from a slightly different angle, which is helpful to our present problem. It may be shown analytically that the influence of the Lorentz polarisation field may alternatively be considered as causing a diminution in the electronic frequencies of the molecules, and consequently an increase of refractivity as required. Assuming that the molecules has only one absorption frequency ν_0 , and that the refractive measurements refer to a frequency ν , the change in ν_0 due to the Lorentz field will be given by

$$\frac{2\nu_0 \delta\nu_0}{\nu_0^2 - \nu^2} = \theta - 1.$$

For alcohol, $n = 1.36$ and $\theta = 1.28$; $\delta\nu_0/\nu_0$ should be considerably less than $(\theta - 1)/2$, and may have about a third or fourth of this value; *i.e.*, $\delta\nu_0/\nu_0 \sim 0.03$. Since the observed shifts of the absorption bands from the vapour to the solution are of this order of magnitude, we may presume that the influence of the physical state is mainly through the refractivity of the medium and the corresponding Lorentz polarisation field acting on the absorbing molecule.

It should be remarked, however, that the intermolecular electric fields, which would be quite large especially in the solid state, may conduce to a Stark splitting of the energy levels of the molecules, and may also be a contributory cause for the observed shifts.

5. Fluorescence Spectra.

The influence of the physical state on *fluorescence* is very similar to that on absorption. Taking for examples fluorene and phenanthrene, the positions of their fluorescent bands for the alcoholic solution and for the solid are entered in Table IV.

TABLE IV.—FLUORESCENCE SPECTRA.

Fluorene.				Phenanthrene.			
Alcoholic Soln.		Solid.		Alcoholic Soln.		Solid.	
ν .	$\Delta\nu$.	ν	$\Delta\nu$	ν .	$\Delta\nu$.	ν .	$\Delta\nu$.
22260		21570		22260		21730	
	1490		1490		1260		1250
23750		23060		23520		22980	
	1400		1380		1280		1220
25150		24440		24800		24200	
	1230		1230		1230		1300
26380		25670		26030		25500	
	1240		1280				
27620		26950					

Here again, just as in absorption, there is a bodily shift of the bands as we pass from the alcoholic solution to the solid state; and the magnitude of the shift is also of the same order as in absorption.

The intervals between the successive fluorescence bands are independent of the physical state, even as the intervals between the absorption bands are. Moreover, the intervals between the fluorescence bands have the same magnitude as the intervals between the corresponding absorption bands.

The positions of the fluorescence bands for solutions of perylene in alcohol, benzene and carbon bisulphide, are given in Table V.

The relative positions of the fluorescence bands in the three solutions are clearly brought out in Fig. 3, in which the three fluorescence spectra are exhibited side by side. As will be seen from Table V. the fluorescence

TABLE V.—FLUORESCENCE OF SOLUTIONS OF PERYLENE.

Solvent.	First Band.	Second Band.
Alcohol . . .	21270	22720
Benzene . . .	21000	22460
Carbon bisulphide	20380	21810

bands shift towards the red by 270 cm.^{-1} as we pass from the alcoholic solution to that in benzene, and again by 890 cm.^{-1} as we pass from the solution in benzene to that in carbon disulphide. The corresponding shifts in the absorption bands of the solutions are 210 and 870 cm.^{-1} respectively.

In conclusion, the author desires to express his grateful thanks to Professor K. S. Krishnan, for his keen interest and constant encouragement in the course of this work.

ABSORPTION OF AIR BY MINERAL OILS.

BY A. GEMANT.

Communicated from the Engineering Laboratory, Oxford University.

Received 13th February, 1936.

1. Introduction.

The purpose of this investigation was to measure the absorption of air by mineral oils in the most important working range of temperature, that is, from 20° to 80° C. Whereas a fairly considerable amount of literature exists on absorption of gases by inorganic as well as organic liquids, some even of recent date,¹ extremely little is known about corresponding data on mineral oils. The reason probably is that since oils do not possess a well-defined composition, reproducible and characteristic data are not to be expected as for liquids with known composition. On the other hand, mineral oils are so important for their application to electrotechnics, that it seemed justifiable to look further into the question. The author is much indebted to Mr. B. L. Goodlet for having raised this suggestion.

Oil is often used in combination with paper or pressboard for impregnated insulating materials. Since air is deleterious to the insulating property of the compound, the oil is degassed before impregnation begins. Degassing usually takes place at about 100° C. ; it is therefore important to know the changes with temperature of the absorption coefficient in the above range.

In the International Critical Tables² a few data for oxygen, nitrogen and hydrogen are published, referring to a transformer oil of Pennsylvanian origin. Whereas there is a fairly large increase of the absorption coefficient from 25° to 80° C. with respect to hydrogen, there is only a slight increase with respect to nitrogen and a slight decrease with regard to oxygen. One would expect a slight increase for air containing roughly 80 per cent. of nitrogen.

In a recent investigation, F. M. Clark³ gives values for the absorption coefficient in oils, which show a definite increase of some 10 per cent. in the temperature range in question.

In the following pages, first the method will be described, followed by a few test measurements on water, in order to check the method. We shall then give the results for several oils and deduce therefrom a general

¹ S. Hamai, *Chem. Soc. Japan Bull.*, 1935, 10, 5.

² *Intern. Crit. Tables*, Vol. III., McGraw-Hill, 1928.

³ F. M. Clark, *Frankl. Inst. J.*, 1933, 215, 39.

rule for the temperature range covered. Finally, we shall add some conclusion drawn from this general result.

2. The Method.

The method for determining the absorption coefficient is in principle a manometric one. The idea was to determine the temperature coefficient of absorption by direct measurement of the difference between the absorbed amounts at 20° and 80° C. The method consisted therefore, in measuring (1) the absolute absorption coefficient at room temperature, (2) the difference between 80° and 20° C.

The first procedure was the following. A glass bulb was filled with approximately 130 c.c. of the oil, the exact mass M of which was determined. The bulb was then connected to a Metropolitan-Vickers low pressure oil pump and evacuated under vigorous shaking for five hours. After exhausting it, the bulb was brought to rest and air let in, and at the same moment the bulb was connected with a mercury manometer, both menisci of which were level. Shaking now commenced, atmospheric and inside pressure being always equalised by lifting one branch of the manometer until both menisci were level. After twenty minutes of shaking, reading of the meniscus was taken, thus determining the volume V of air absorbed by the oil. The Bunsen absorption coefficient (volume of gas reduced to normal pressure and 0° C., absorbed by 1 c.c. of oil at a partial pressure of the gas of 760 mm. mercury) is given by :

$$\alpha = \frac{T_0}{T} \frac{V}{\nu M} \quad \dots \quad (1)$$

where T = absolute temperature of air, $T_0 = 273.1$ and ν = specific volume of oil.

The determination of the volume difference ν , corresponding to the different absorption between 20° and 80° C., $V_{80} - V_{20}$, was carried out in the following way. The open bulb, containing the oil, was placed in an oil bath of 80° C. and shaken for twenty minutes, so that absorption equilibrium was reached. The oil was then brought to rest and the hot oil of the bath quickly replaced by cold oil. After this procedure, a pause of two hours followed (with the bulb still open) in order to ensure complete thermal equilibrium at room temperature. Preliminary measurements showed that this is reached in practically half an hour. Then the bulb was connected with the manometer, shaking begun and the volume difference ν determined. Since a certain amount of absorption takes place during the two hours of waiting, a preliminary measurement of the rate of absorption was taken with the bulb at rest. The absorbed percentage for the first two hours (with a completely degassed oil) has been added as correction term to the difference value ν .

3. Test Measurements with Water.

In order to see whether the apparatus and the method work satisfactorily, some test measurements with water have been carried out, the absorption coefficients of which are known. Since the vapour pressure of water is comparable with that of the air, formula (1) has to be modified for this case. If the vapour pressure of water at room temperature is p , we have for the reduced volume of the gas,

$$\frac{T_0}{T} \frac{P - p}{P_0} V.$$

If, on the other hand, the vapour pressure at the bath temperature is p' , the quantity

$$\frac{T_0}{T} \frac{P - p}{P_0} \frac{V}{\nu M}$$

will give the absorption coefficient at a partial pressure of the air $P - p'$. Its value at the normal pressure P_0 is therefore

$$\alpha = \frac{T_0}{T} \frac{P - p}{P - p'} \frac{V}{vM} \quad (2)$$

instead of (1).

First a few absolute measurements were taken, which are tabulated in Table I. In the first column is given the atmospheric pressure P in mm. mercury (where necessary), in the second the room temperature t in degrees Centigrade. The third column contains the bath temperature t' in degrees Centigrade, the fourth the mass M of the water, and the fifth the volume absorbed, V . The absorption coefficient α calculated by means of (2) follows, compared with its value known from the literature. To compute the latter, the International Critical Tables have been used, which contain the values for K , Henry's law constant, as measured by Winkler. α was calculated from K by means of the formula

$$\alpha = \frac{0.95 \times 10^6}{K}.$$

TABLE I.—ABSOLUTE TEST MEASUREMENTS WITH WATER.

P in mm. Mercury.	t in °C.	t' in °C.	M in gr.	V in c. c.	α Calculated.	α (Winkler).
—	22.4	22.4	115.35	2.13	0.0170	0.0180
—	22.4	22.4	163.80	3.03	0.0170	0.0180
758	26	42.5	151.7	2.13	0.0134	0.0139

As can be seen, the measured and known values of α agree within 5 per cent., which is satisfactory for our purpose.

Two test measurements for the difference method follow, which is even more important from the standpoint of the oil measurements. Table II. contains the atmospheric pressure, the room temperature, the two respective bath temperatures, the mass of the water and the measured volume difference v . In the last column there is the value of v as calculated from the known values of α and using the following equation, deduced from (2) :

$$v = \frac{T}{T_0} \frac{M}{P - p} [(P - p_1') v_1 \alpha_1 - (P - p_2') v_2 \alpha_2] \quad (3)$$

In this equation the indices 1 and 2 refer to the two bath temperatures.

TABLE II.—DIFFERENCE TEST MEASUREMENTS WITH WATER.

P in mm. Mercury.	t in °C.	t_1' in °C.	t_2' in °C.	M in gr.	v Measured.	v (Computed from Values for α of Winkler).
761	25	23	43	143.22	0.72	0.73
745	18	20	40	129.3	0.73	0.69

The agreement is again satisfactory.

4. Results on a Special Oil Sample.

Before giving the summarised results on different oil samples, we indicate the detailed results on a special oil (No. 2 of the list in Table III.). First the specific volume had to be measured as a function of temperature.

Fig. 1 shows the result as a straight line between 10° and 100° . The absolute measurement is indicated in Fig. 2. The abscissæ are minutes from the beginning of shaking and the ordinates c.c. of air passing into the oil. In eight minutes the final value

$$V_{18} = 12.62$$

was reached. Using equation (1), we have for 18° C.

$$\alpha_{18} = 0.088.$$

As to the difference measurements between 18° C. and 80° C., two measurements were taken, one with two hours waiting for equilibrium, yielding 0.51 c.c.; another with three hours waiting, yielding 0.45 c.c. These data have to be corrected for the waiting time.

Fig. 3 shows the absorption rate with the oil in rest, the abscissæ being again minutes, the ordinates c.c. In one hour the absorbed amount is 11.5 per cent. of the total; in two hours, 20.6 per cent., which corresponds

to a value of 28.6 per cent. for three hours (assuming the function to be exponential). The corrected values are respectively 0.64 c.c. and 0.63 c.c., showing a good agreement. This means that $V_{80} = 13.25$ c.c.

From equation (1) it is easy to deduce

$$\alpha_2 = \frac{V_2 v_1}{V_1 v_2} \alpha_1 \quad (4)$$

The factor of α_1 in this equation should be called $(1 + k)$, if α_1 refers to room temperature and α_2 to 80° C. The value of k will indicate directly the temperature variation of the absorption-coefficient. Apply-

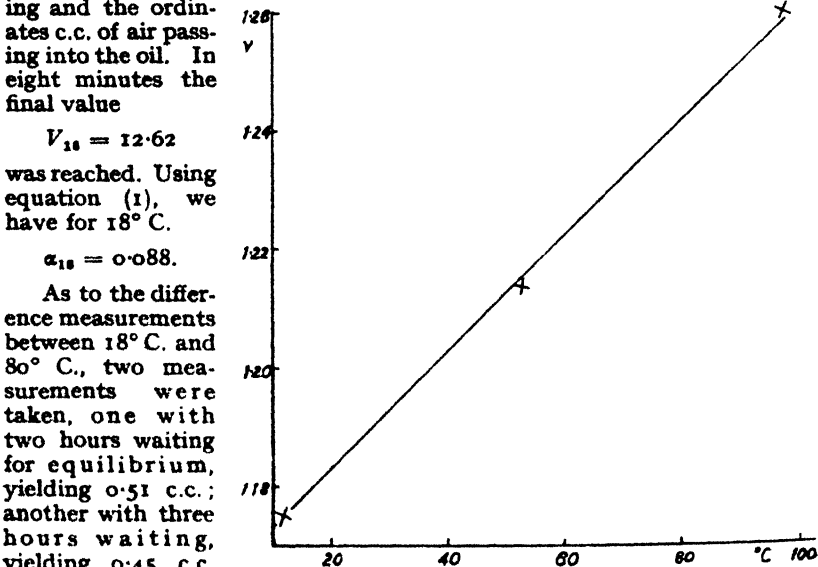


FIG. 1.—Specific volume (v) as function of temperature. (Oil Nr. 2.)

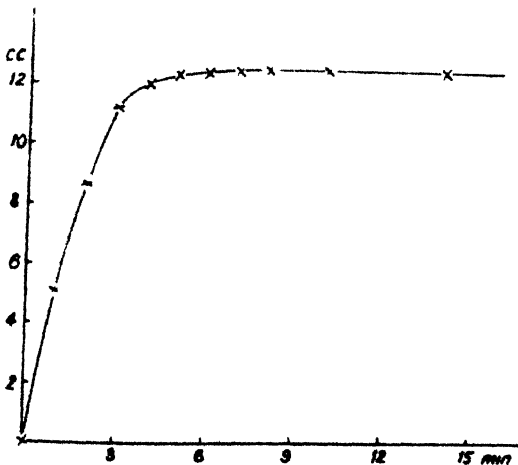


FIG. 2.—Absorbed volumes of air as function of time. Oil shaken. (Oil Nr. 2.)

ing (4) to our case above, we get

$$k = -0.002,$$

indicating a difference in α between 18 and 80° C. of 0.2 per cent.

Assuming v to be correct to 10 per cent., which is justifiable according to the test with water, we may conclude that the difference between α_{10} and α_{20} is certainly not greater than roughly $\frac{1}{2}$ per cent.

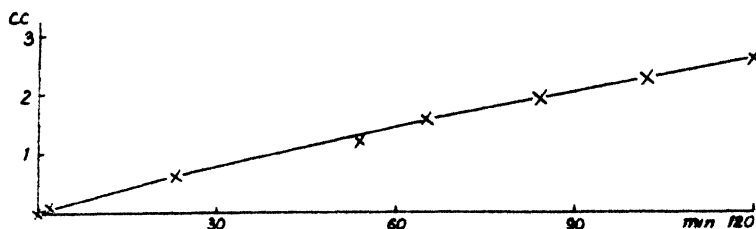


FIG. 3.—Absorbed volumes of air as function of time.
Oil in rest.
(Oil Nr 2.)

5. Results on Several Oils.

In Table III. the eight samples of oil which have been investigated are characterised either by some data concerning their origin and grade or else, if such were not available, by their viscosity at 20° and 60° C.

TABLE III.—DATA OF OILS INVESTIGATED.

No.	Supplied by	Origin of Oil.	Grade to British Standard Specification	Viscosity Data in Poise.
1	Silvertown Lubricants	Russia	A. 30	---
2	"	America : Kansas, Oklohama	A. 0	---
3	"	Russia	B. 30	---
4	"	America : Pennsylvania	B. 0	---
5	"	---	A. 30	23°, 0.21 ; 58°, 0.070
6	Shell-Mex and B.P.	---	---	21°, 0.060 ; 60°, 0.022
7	"	---	---	21°, 2.0 ; 60°, 0.21
8	Vacuum Oil Co.	---	---	" Mobiloil BB "

Whereas the first six varieties were more or less light oils, the last two were chosen as of the more viscous type. Table IV. includes the results obtained from these eight samples by means of the procedure outlined above. The first column contains the number of the oil in accord with Table III. ; the second the lower bath temperature, which varied according to the room temperature (the higher temperature was always 80° C.) ; the third M , the mass of the oil ; the fourth and fifth the two respective specific volumes v_1 and v_2 . The total air volume V , and the difference volume v come next, followed by α at room temperature and h according to equation (4).

Apart from samples 6 and 7, none of the values of h exceed a few tenths per cent. But since h for oil 6 is -2 per cent. (temperature coefficient negative), and for oil 7 $+2$ per cent. (temperature coefficient positive), these somewhat higher values do not seem to be of great importance. Considering the bulk of the results, and allowing for 0.5 per cent. error in

TABLE IV.—ABSORPTION RESULTS ON OILS MEASURED (BETWEEN t_1 and 80° C.).

No.	t_1 .	M .	v_1 .	v_2 .	V .	v .	a_1 .	k .
1	10	108.95	1.164	1.225	12.48	0.64	0.092	— 0.001
2	18	113.0	1.181	1.243	12.62	0.63	0.088	— 0.002
3	15	111.35	1.154	1.214	12.04	0.66	0.088	+ 0.001
4	16	108.60	1.176	1.239	12.00	0.55	0.088	— 0.005
5	20	107.3	1.165	1.224	12.25	0.52	0.092	— 0.007
6	20	106.2	1.211	1.280	14.70	0.45	0.106	— 0.022
7	20	115.3	1.083	1.135	9.80	0.66	0.073	+ 0.020
8	20	111.6	1.139	1.189	10.60	0.46	0.078	— 0.003

k , we may express the result by saying that the temperature variation of the absorption coefficient is practically zero between 20° and 80° C.; at all events, generally not greater than roughly 1 per cent.

Taking the difference in absorbed air volume per mass unit of oil, the temperature coefficient is of the order of ± 5 per cent. But this coefficient is practically identical with the corresponding volume expansion. Although a given mass of oil absorbs 5 per cent. more air at 80° than at 20° C., the absorbed amount per volume unit of oil is practically the same at both temperatures.

As to the absolute amount α_1 , the results are in agreement with earlier observations, as well as to its general order of 10 per cent. and to its decreasing with increasing viscosity of the oil. (Oils 7 and 8 have the highest viscosity, oil 6 the lowest, in the series.)

6. Thermodynamic Conclusions.

Applying the second law of thermodynamics to the absorption process, the equation

$$\frac{d \ln \lambda}{dT} = - \frac{Q}{RT^2} \quad . \quad . \quad . \quad (5)$$

is obtained. Here λ is the Ostwald absorption coefficient, which is related with α by

$$\alpha = \frac{T_0}{T} \lambda.$$

Q is the molar latent heat of absorption. Equation (5) allows us to compute the temperature coefficient of α in terms of the latent heat.

Suppose that the absorption is a purely physical process, and that no interchange whatever occurs between the molecules of the solvent and that of the gas. This means that the increase in total energy U during absorption of one mol of a gas is zero; since

$$U = A - Q,$$

where A = the maximal work,

$$Q = A \quad . \quad . \quad . \quad (6)$$

But A is known, if λ is known, since

$$A = RT \ln \lambda \quad . \quad . \quad . \quad (7)$$

Combining (5) and (7), we have

$$\frac{d \ln \lambda}{dT} = - \frac{\ln \lambda}{T} \quad . \quad . \quad . \quad (8)$$

Thus, for $\lambda > 1$, the temperature coefficient of λ ought to be negative, with $\lambda < 1$ negative. However, it is easy to show that equation (8) is not fulfilled at all in the case of oil and air. λ is of the order of 0.1, which

means that $\frac{d \log_{10} \alpha}{dt}$ ought to be of the order of 0.003, whereas our experiments indicate that it is less than 0.00007.

In comparison, it may be shown that (8) is approximately fulfilled in the case of hydrogen and oil (taken from the data in the International Critical Tables). The mean value for α appears to be 0.06, yielding for the right side of (8) 0.0036. Since α increases from 0.051 at 25° to 0.069 at 80°, the left side of (8) appears to be 0.0024,—the same order as the right.

In other words, hydrogen fulfils (8) and therefore (6), indicating a purely physical absorption. Air, and especially oxygen (see the Introduction), on the other hand, do not fulfil (6), indicating a certain interchange between the oil and gas molecules.

Assuming, therefore,⁴ that this interchange is involved with a certain drop q in the total energy, we obtain in place of (6)

$$Q = A + q \quad (9)$$

Whereas it does not seem clear what kind of interchange may occur with nitrogen, there is no difficulty in explaining the effect with oxygen as a kind of reversible oxidation, forming for instance some labile peroxides with traces of acids always present in oils. Since the experiments indicate Q to be very small, it follows from (9) that q must be of the order of A , which is given by (7).

The conclusion reached is, therefore, that oxygen undergoes a secondary reversible chemical reaction immediately after absorption, and that the latent heat of this reaction is of the order of $RT \ln \lambda$. This conclusion is supported by an investigation by the author on the oxidation of mineral oils, which is now in progress.

7. Electrotechnical Conclusions.

There is first a remark to be made concerning the degassing of an oil preceding the impregnation process. Since the absorption coefficient is independent of temperature, the heating of the oil during degassing has itself no expelling effect whatsoever, as is sometimes thought. It is only useful in that it helps in removing the water and accelerates the new equilibrium under vacuum.

A second point which has to be discussed, concerns the temperature variation of the breakdown strength of oil. It is known that the latter usually increases with temperature in the range concerned. Clark observed—as already mentioned—a finite increase of α in the same range and developed a theory⁵ which explains the former effect directly by the latter, by assuming that the breakdown strength varies proportionally to the square root of the air content of the oil. In spite of the apparent aptitude of this assumption to explain several observations concerning the variation of the breakdown strength, there are several objections which have to be raised:—

(1) Mainly it should be emphasised that our experimental results indicate an absorption coefficient independent of temperature, although the oils under investigation show the breakdown effect just as well as other oils, as break-down tests with oils Nos. 1–4, between 20 and 80° C. revealed.

⁴ G. Tammann, *Z. anorg. Chem.*, 1926, 158, 17.

⁵ F. M. Clark, *Electrical Engineering*, 1935, 54, 50.

(2) Our results show how very slowly the equilibrium is reached when the oil is in rest. Now the temperature change in the breakdown effect is immediately observable, after the temperature of the oil has been raised or lowered, although no appreciable change in the absorption equilibrium could have taken place during this short time.

(3) Several authors stressed the point that completely dry oil does *not* show the temperature-breakdown effect at all. This was proved recently by A. Lazarev,⁶ who found that the breakdown strength of thoroughly dry oil decreases slightly but continuously with an increase of temperature. The peculiar curve obtained with wet oils can be explained by assuming an equilibrium between water in colloidal and in molecular solution, the second state being preferred at higher temperatures. That colloidal water is more deleterious than dissolved water is well known.⁷

Summary.

(1) An apparatus and a method are described, based on the manometric principle, to measure the absorption of gases by liquids and its temperature coefficient. They are utilised here in measuring the absorption of air in mineral oils for 20° and 80° C.

(2) It appears from results obtained from different oils that the Bunsen absorption coefficient, referring to the volume unit of oil, is practically constant in the above range of temperature, the variation generally not being larger than 1 per cent.

(3) Thermodynamical conclusions from the above result indicate that the absorption of air in oil is followed by a first step of reversible oxidation process.

(4) Some conclusions are drawn as to the temperature variation of the electrical breakdown strength of oil.

The author is much indebted to Professor R. V. Southwell, F.R.S., for facilities in the Engineering Laboratory, Oxford, and to Messrs. Metropolitan-Vickers Electrical Co., Ltd., for a grant enabling him to carry out this work. Further thanks are due to Messrs. Silvertown Lubricants Ltd., and to Messrs. Shell-Mex and B.P. Ltd., for generous samples of oil put at the author's disposal.

⁶ A. Lazarev, *Technical Physics of the U.S.S.R.*, 1934, 1, 169.

⁷ A. Gemant, *Liquid Dielectrics*, p. 139. New York, 1933.

MAGNETIC SUSCEPTIBILITY AND OTHER PROPERTIES OF BINARY MIXTURES OF ORGANIC LIQUIDS.

BY V. C. G. TREW AND J. F. SPENCER.

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In a previous investigation,¹ it was shown that the physical properties of mixtures of liquids of a chemically dissimilar type, between which there is the possibility of combination, exhibit more marked deviations from

¹ "Some Physical Properties of Mixtures of Certain Organic Liquids," Trew and Watkins, *Trans. Faraday Soc.*, 1933.

the mixture law than mixtures of chemically similar liquids such as the members of an homologous series, but that even in the latter case considerable deviations do occur. In the present communication, some further binary mixtures are considered, in order to determine whether any general rule can be deduced connecting such deviations with differences in chemical constitution of the liquids mixed. It was thought that differences in molecular weight, and hence size of molecule, of the constituents might be a factor causing deviations from the mixture law. In addition, the presence of positive and negative groups might also contribute to such deviations.

Two groups of mixtures were investigated, the first consisting of mixtures of the aromatic hydrocarbons, benzene and toluene with *meta*-cresol and, for purposes of comparison, a set of mixtures of benzene and toluene. In the second group, mixtures of aniline with *meta*-cresol, nitrobenzene with *meta*-cresol and aniline with nitro benzene were investigated. Measurements of density, specific heat, heat of mixing, refractive index and magnetic mass susceptibility were made.

Experimental.

A.R. materials were employed throughout, and these were then carefully dried and fractionated until a constant boiling fraction was obtained.

TABLE I.—BOILING-POINTS AND DENSITIES OF PURE LIQUIDS.

Liquid.	Pressure.	Boiling-Pt.	Density D_4^{20} .
Benzene . .	758 mm.	80.5° C.	0.8708
Toluene . .	753 ..	111.0° C.	0.8565
Aniline . .	760 ..	184.0° C.	1.0148
Nitrobenzene .	762 ..	210.6° C.	1.1937
<i>Meta</i> -cresol .	760 ..	202.4° C.	1.0292

The density of the pure liquids was determined, using a standard pyknometer, and was used as a criterion of purity, the values being compared with those given in the *International Critical Tables*. Table I. shows the physical constants obtained for each of

the constituent liquids.

A series of mixtures was then made up, as previously described,^{1,2} containing varying weights of the two components, the proportion of each being expressed as moles per cent. of the total composition. The methods employed for the determination of the density, refractive index, and thermal properties were as described previously. The molecular refractivity was calculated from the refractive index, using the Lorentz and Lorenz formula

$$R = \frac{\mu^2 - 1}{\mu^2 + 2} \cdot \frac{m}{d} \text{ where } m \text{ is the molecular weight of the constituent liquid}$$

when pure, or in the case of a mixture, the mean molecular weight. The molar magnetic mass susceptibility was calculated from the magnetic mass susceptibility measured by the method previously described.¹ The results are summarised in the following tables. Tables II. to IV. give the values obtained for the various properties, while in Table V. the maximum percentage deviation has been recorded for each property investigated, with the exception of the specific heat which was not measured to a sufficient degree of accuracy to give comparative values.

^{1,2} "Physical Properties of Mixtures of Acetone and Bromoform," Trew, *Trans. Faraday Soc.*, 1932.

TABLE II.—DENSITY, D_4^{20} , REFRACTIVE INDEX AND MOLECULAR REFRACTIVITY.

Mixture.	Composition. Mols. Per Cent. of Second Constituent.	Density D_4^{20} .	Refractive Index n_D^{20} .	Mol. Refractivity.
Benzene—Toluene.				
Benzene	0	0.8702	1.49591	26.16
I.	8.5	0.8676	1.49519	26.63
II.	18.2	0.8670	1.49422	27.05
III.	26.4	0.8656	1.49384	27.48
IV.	35.7	0.8636	1.49327	27.95
V.	45.5	0.8606	1.49277	28.49
VI.	55.8	0.8592	1.49213	28.98
VII.	65.9	0.8586	1.49161	29.46
VIII.	76.8	0.8582	1.49098	29.98
IX.	88.1	0.8570	1.49074	30.53
Toluene	100.0	0.8563	1.49030	31.07
Benzene—<i>m</i>-Cresol.				
Benzene	0	0.8702	1.49591	26.16
I.	8.8	0.8878	1.50044	26.75
II.	17.6	0.9026	1.50525	27.38
III.	26.3	0.9177	1.50934	27.97
IV.	35.6	0.9350	1.51419	28.57
V.	45.1	0.9497	1.51869	29.22
VI.	56.0	0.9672	1.52319	29.95
VII.	66.1	0.9806	1.52629	30.63
VIII.	76.8	0.9977	1.53150	31.34
IX.	88.0	1.0142	1.53491	32.05
Cresol	100.0	1.0293	1.53812	32.84
Toluene—<i>m</i>-Cresol.				
Toluene	0	0.8562	1.49030	31.07
I.	12.5	0.8786	1.49663	31.29
II.	16.1	0.8847	1.49937	31.38
III.	31.0	0.9111	1.50620	31.61
IV.	41.5	0.9307	1.51133	31.77
V.	47.4	0.9401	1.51430	31.91
VI.	57.6	0.9570	1.51920	32.10
VII.	68.6	0.9754	1.52441	32.32
VIII.	77.0	0.9906	1.52787	32.45
IX.	89.1	1.0082	1.53329	32.74
Cresol	100.0	1.0292	1.53812	32.84
Aniline—Nitrobenzene.				
Aniline	0	1.015	1.58170	30.57
I.	8.7	1.031	1.57832	30.79
II.	18.2	1.048	1.57458	31.03
III.	27.7	1.068	1.57117	31.16
IV.	37.0	1.086	1.56778	31.42
V.	47.0	1.104	1.56478	31.61
VI.	58.0	1.123	1.56102	31.88
VII.	66.1	1.136	1.55875	32.04
VIII.	78.1	1.157	1.55518	32.32
IX.	89.1	1.176	1.55365	32.61
Nitro- Benzene	100.0	1.194	1.54928	32.73

TABLE II. (continued).

Mixture.	Composition. Mols. Per Cent. of Second Constituent.	Density D_4^{25} .	Refractive Index n_D^{25} .	Mol. Refractivity.
Aniline—<i>m</i>-Cresol.				
Aniline	0	1.0147	1.58170	30.57
I.	12.2	1.0187	1.57577	30.80
II.	13.7	1.0192	1.57502	30.85
III.	22.0	1.0212	1.57117	30.99
IV.	37.1	1.0232	1.56431	31.33
V.	45.4	1.0273	1.56075	31.45
VI.	57.3	1.0278	1.55579	31.77
VII.	66.2	1.0281	1.55187	31.96
VIII.	77.6	1.0287	1.54692	32.27
IX.	88.6	1.0290	1.54228	32.52
<i>m</i> -Cresol	100.0	1.0293	1.53812	32.84
Nitrobenzene—<i>m</i>-Cresol.				
Nitrobenzene	0	1.194	1.54928	32.73
I.	10.1	1.177	1.54794	32.78
II.	19.3	1.162	1.54685	32.76
III.	29.3	1.144	1.54560	32.82
IV.	39.2	1.128	1.54503	32.83
V.	51.5	1.108	1.54387	32.85
VI.	59.1	1.097	1.54282	32.80
VII.	69.2	1.081	1.54166	32.76
VIII.	78.8	1.063	1.54029	32.85
IX.	89.9	1.045	1.53860	32.81
Cresol	100.0	1.029	1.53812	32.84

TABLE III.—THERMAL DATA (SPECIFIC HEAT, HEAT OF MIXING, MOLECULAR HEAT).

Mixture.	Composition. Mols. Per Cent. of Second Constituent.	Specific Heat.	Heat of Mixing (Absorbed). Calories per Gram.	Molecular Heat.
Benzene—Toluene.				
Benzene	0	0.474	—	37.1
I.	19.6	0.449	0.119	36.3
II.	37.6	0.426	0.228	35.5
III.	52.9	0.415	0.279	35.5
IV.	69.3	0.413	0.228	36.2
V.	85.0	0.410	0.145	36.9
Toluene	100.0	0.383	—	35.3
Benzene—<i>m</i>-Cresol.				
Benzene	0	0.474	—	37.0
I.	24.3	0.455	2.05	38.8
II.	40.4	0.452	2.53	40.7
III.	69.8	0.479	2.39	47.4
IV.	76.7	0.487	2.28	49.2
V.	88.9	0.464	1.60	48.7
Cresol	100.0	0.515	0.00	55.6

TABLE III. (continued).

Mixture.	Composition. Mols. Per Cent. of Second Constituent.	Specific Heat.	Heat of Mixing (Absorbed). Calories per Gram.	Molecular Heat.
Toluene—<i>m</i>-Cresol.				
Toluene	0	0.383	—	35.3
I.	21.3	0.408	1.68	39.0
II.	38.6	0.425	2.02	41.8
III.	56.9	0.436	2.05	44.1
IV.	72.7	0.441	1.45	45.7
V.	87.1	0.456	0.80	48.3
Cresol	100.0	0.515	—	55.6
Aniline—Nitrobenzene.				
Aniline	0	0.448	—	41.71
I.	23.5	0.443	0.85	44.36
II.	43.9	0.426	1.24	45.28
III.	61.4	0.394	1.22	43.92
IV.	75.8	0.383	1.11	44.35
V.	90.0	0.367	0.55	44.08
Nitrobenzene	100.0	0.355	—	43.69
Aniline—<i>m</i>-Cresol.				
Aniline	0	0.448	—	41.7
I.	17.1	0.462	1.97 *	44.2
II.	39.9	0.473	3.88 *	46.5
III.	52.9	0.493	4.85 *	46.8
IV.	68.7	0.463	4.66 *	47.9
V.	84.8	0.463	3.06 *	48.4
Cresol	100.0	0.515	—	55.0
Nitrobenzene—<i>m</i>-Cresol.				
Nitrobenzene	0	0.355	—	43.7
I.	13.8	0.381	1.00	46.0
II.	26.3	0.395	1.27	47.0
III.	42.5	0.416	1.30	48.5
IV.	60.4	0.449	1.03	51.2
V.	79.0	0.490	0.57	54.5
Cresol	100.0	0.515	—	55.0

* Heat evolved.

TABLE IV.—DENSITY D_4^{25} , MAGNETIC SUSCEPTIBILITY, MOLECULAR SUSCEPTIBILITY.

Mixture.	Composition. Mols. Per Cent. of Second Constituent.	Density D_4^{25} .	Magnetic Susceptibility — 10^6 X.	Molecular Susceptibility — 10^6 X.M.
Benzene—Toluene.				
Benzene	0	0.8722	0.710	55.4
I.	6.40	0.8710	0.711	56.2
II.	15.35	0.8692	0.714	57.3
III.	34.17	0.8668	0.719	59.6
IV.	45.44	0.8640	0.720	60.6
V.	52.58	0.8630	0.721	61.6
VI.	59.80	0.8626	0.723	62.5
VII.	67.77	0.8616	0.724	63.4
Toluene	100.00	0.8586	0.728	67.0

TABLE IV. (continued).

Mixture.	Composition. Mols. Per Cent. of Second Constituent.	Density D_{4}^{20} .	Magnetic Susceptibility — $10^6 X$.	Molecular Susceptibility — $10^6 XM$.
Benzene—<i>m</i>-Cresol.				
Benzene	0	0.8722	0.710	55.4
I.	10.65	0.8916	0.705	57.3
II.	26.04	0.9182	0.696	59.8
III.	40.73	0.9422	0.692	62.5
IV.	46.78	0.9510	0.689	63.5
V.	58.06	0.9670	0.685	65.4
VI.	73.64	0.9892	0.677	67.8
VII.	88.67	1.0051	0.671	70.2
Cresol	100.00	1.0302	0.672	72.6
Toluene—<i>m</i>-Cresol.				
Toluene	0	0.8586	0.728	67.0
I.	11.32	0.8788	0.718	67.4
II.	22.24	0.8978	0.710	67.9
III.	33.94	0.9186	0.705	68.7
IV.	45.06	0.9386	0.699	69.4
V.	54.66	0.9556	0.694	69.9
VI.	76.12	0.9922	0.683	71.2
VII.	87.74	1.0120	0.675	71.6
Cresol	100.00	1.0302	0.672	72.5
Aniline Nitrobenzene.				
Aniline	0	1.018	0.662	61.6
I.	12.18	1.040	0.641	62.0
II.	26.55	1.066	0.614	62.0
III.	39.85	1.092	0.588	61.8
IV.	50.37	1.111	0.571	61.8
V.	59.00	1.127	0.561	62.1
VI.	72.83	1.150	0.537	61.7
VII.	87.83	1.177	0.520	62.0
Nitrobenzene.	100.00	1.198	0.502	61.8
Aniline—<i>m</i>-Cresol.				
Aniline	0	1.0182	0.662	61.6
I.	12.05	1.0214	0.663	62.9
II.	26.79	1.0250	0.665	64.5
III.	42.75	1.0273	0.668	66.4
IV.	47.88	1.0282	0.669	66.9
V.	57.46	1.0309	0.670	68.1
VI.	75.13	1.0315	0.671	70.0
VII.	87.62	1.0303	0.671	71.3
Cresol	100.00	1.0302	0.672	72.6
Nitrobenzene—<i>m</i>-Cresol.				
Nitrobenzene	0	1.198	0.502	61.8
I.	12.98	1.176	0.522	63.2
II.	27.20	1.152	0.543	64.6
III.	41.48	1.128	0.566	66.1
IV.	47.90	1.117	0.578	67.0
V.	57.78	1.103	0.593	67.8
VI.	73.20	1.075	0.620	69.5
VII.	87.86	1.051	0.650	71.3
Cresol	100.00	1.030	0.672	72.6

TABLE V.—MAXIMUM PERCENTAGE DEVIATION.

Mixture.	Density D_4^{25} .	Density D_4^{28} .	Refractive Index.	Magnetic Mass Susceptibility.	Molar Refractivity.	Molar Susceptibility.	Heat Evolved.
Benzene—Toluene	-0.2	-0.3	-0.06	-0.2	+0.26	<0.1	-0.36
Benzene— <i>Meta</i> -cresol	+0.5	+0.9	+0.25	+0.5	+0.26	<0.1	-2.80
Toluene— <i>Meta</i> -cresol	+0.3	+0.3	+0.13	+0.4	±0	+0.1	-2.08
Aniline—Nitrobenzene	+0.2	+0.4	-0.15	+1.8	+0.13	-0.1(5)	-1.25
Aniline— <i>Meta</i> -cresol	+0.4	+0.5	-0.10	-0.1	-0.39	<0.1	+4.80
Nitrobenzene— <i>Meta</i> -cresol	±0	±0	+0.05	+1.1	±0	<0.1	-1.30

Discussion of Results.

1. Binary Mixtures from Benzene, Toluene and *m*-Cresol.

Examination of Table V. shows that, for all properties, slight deviations from the mixture rule are obtained, even for such chemically similar pairs of liquids as benzene and toluene. Density deviations at 28° C., were for all mixtures greater than for the lower temperature, 25° C. The results for these three mixtures show a close similarity in the direction of the deviation obtained in the case of most of these properties. The deviations in density, refractive index and magnetic mass susceptibility for the mixtures of the hydrocarbons with *m*-cresol are all of the same sign, indicating that the causes of deviation are probably similar for these properties, in both mixtures. Benzene and *m*-cresol mixtures show greater deviations in all properties than do toluene and *m*-cresol. This suggests that when other factors, such as chemical dissimilarity, are absent, the deviations are smaller the closer the molecular weights of the components are to one another. It seems also likely that the smaller deviation on mixing toluene and *meta*-cresol can be accounted for by the greater similarity of their molecular structure, that is, the presence of the methyl group in both. The shape of the toluene molecule would thus be more like that of the cresol, than would that of benzene.

2. Binary Mixtures from Aniline, Nitrobenzene and *m*-Cresol.

A marked change of colour was observed on mixing aniline and nitrobenzene, even in the absence of light, suggesting that some considerable change had taken place on mixing these liquids. The deviations obtained, however, were no greater than for other mixtures, indicating that any change is due to association, rather than to a definite chemical combination. The nitrobenzene—*m*-cresol mixture appears to be nearly ideal, a somewhat unexpected result in view of the nature of the constituent molecules. Unlike the first group of mixtures, there seems in these three sets of mixtures to be no simple common factor causing deviations since Table V. shows no relationship between the direction of the deviations for the properties investigated. It must therefore be concluded that deviations here are due to more than one determining factor.

General.

The most important general result brought out by a consideration of columns 4 and 6 of Table V. is that for the six sets of mixtures the molar magnetic susceptibility is more nearly an ideal property than the mass susceptibility from which it is calculated. This is fully in keeping with the theoretical view that diamagnetic susceptibility is a fundamental atomic property.

Summary.

(1) The density, refractive index, heat of mixing, specific heat and magnetic mass susceptibility of a series of mixtures of the liquids benzene, toluene, *m*-cresol, aniline and nitrobenzene have been measured.

(2) None of the pairs of liquid mixtures can be considered as ideal with the possible exception of the nitrobenzene—*m*-cresol mixture which showed least deviation from the mixture law.

(3) Similar deviations were obtained for different properties for mixtures of benzene and toluene, respectively, with *m*-cresol, the wider apart the molecular weights of the constituents the more marked the deviation.

(4) For mixtures of nitrobenzene and aniline, respectively, with *meta*-cresol, no general rule governing the deviation of the properties investigated could be discovered.

(5) The molar magnetic mass susceptibility proved to be a more nearly additive property than any other property investigated.

The authors desire to express their thanks to Miss J. Cattermole, for carrying out the measurements of refractive index, density at 28°, specific heat and heat of mixing recorded in this paper.

One of us (V. C. G. T.), desires to express thanks to the Council of the Chemical Society for a grant which partially defrayed the cost of materials.

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CALCULATION OF THE RATE OF ELEMENTARY REACTIONS OF LIGHT AND HEAVY HYDROGEN.

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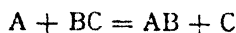
1.

The reactions which will be the subject of the present paper are as follows :

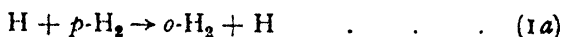


The first two reactions determine the rate of homogeneous thermal conversion of light and heavy *para-ortho*-hydrogen. The mechanism of the homogeneous thermal conversion of light *para*-hydrogen into ordinary hydrogen has been cleared up in an important paper by A. Farkas.¹ The rates of reaction (2) together with those of (3) and (4) have been measured recently by A. and L. Farkas² and compared with each other on the basis of the usual theory of collision numbers. In the present paper we shall compute the reaction rate of the *elementary reactions* (1) to (4) on the basis of more recent theories^{3, 4, 5} since, so far, these are the only examples providing both theoretical and experimental data for a comparison.

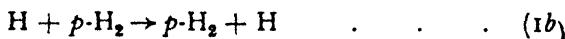
It will be interesting to calculate theoretically the number of interchanges which take place per unit time and volume (sec. litre) and unit concentration (mol./litre) of the reagents (H and H₂ *e.g.*). We designate as interchange a reaction involving atoms and molecules of the general type



where A, B and C represent H or D atoms. The rate of interchange can be measured directly, in principle, in cases (3) and (4). In reaction (1) only the rate of conversion :



can be measured directly. In the number of interchanges, as defined before, however, the reaction :



should also be counted. The number of these is 1/3 of those which lead to the *ortho*-molecule, strictly according to their statistical weights.⁶ The total number of atomic interchanges is, thus, 4/3 times the number of *para-ortho*-conversions. Similarly the number of interchanges in case (2) is three times greater than the number of *ortho-para*-conversions, which can be measured directly in this case.²

The results for the rates of the first two interchange reactions are as follows :

TABLE I.

T.	k_1 .	k_2 .
283 ⁷	1.3×10^4	—
373 ⁷	3.1×10^5	—
873	1.37×10^9	0.70×10^9
930	1.71×10^9	0.88×10^9
973	2.00×10^9	1.02×10^9
1023	2.38×10^9	—

¹ A. Farkas, *Z. Elektrochem.*, 1930, **36**, 782; *Z. physik. Chem.* 1931, **10B**, 419.

² A. Farkas and L. Farkas, *Proc. Royal Soc., A*, 1935, **152**, 124.

³ Pelzer and Wigner, *Z. physik. Chem.*, 1932, **15B**, 445.

⁴ E. Wigner, *ibid.*, **19B**, 203.

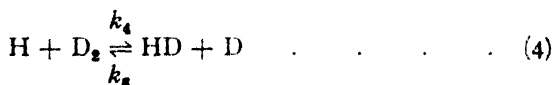
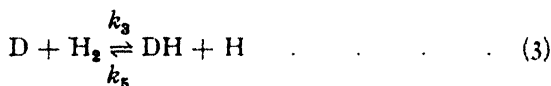
⁵ Eyring, *J. Chem. Physics*, 1935, **3**, 107; E. Evans and M. Polanyi, *Trans. Faraday Soc.*, 1935, **31**, 875.

⁶ A. Farkas, "Ortho-hydrogen, para-hydrogen and heavy hydrogen," Cambridge, 1935, p. 66.

⁷ K. H. Geib and P. Harteck, *Z. physik. Chem.*, 1931, *Bodensteinband*, p. 849.

The ratio of the reaction rates of (1) and (2) according to Table I. is about 1.95. This differs somewhat from the ratio given previously² (which was 1.8) since the higher D atom concentration in 95 per cent. *o*-D₂ compared with that in ordinary D₂ is now taken into account. The increase of the H atom concentration in 50 per cent. *p*-H₂, which was used in the experiments on the conversion *p*-H₂ → *o*-H₂, can be neglected. The increase of H and D atom concentration in *p*-H₂ and *o*-D₂ respectively is due to the comparatively low entropy of these gases.

In the case of reactions (3) and (4) it is not possible from the present data, to calculate both k_3 and k_4 separately; only one equation for k_3 and k_4 can be derived. The reaction investigated was the formation of HD from H₂ and D₂ which had the mechanism:



The content of HD in the reacting mixture was measured as function of time under different pressures and temperatures. The velocity constants of the three dissociation reactions will be denoted by k_{ds} , $k_{d\alpha}$, k_{da} that of the reverse, recombination reaction (which occurs at triple collisions) by k_{rs} , $k_{r\alpha}$, k_{ra} . The constants of the reactions (3) and (4) are k_3 and k_4 in the sense from left to right, and k_5 and k_6 in the reverse sense. Since the number of atoms is certainly low compared to the number of molecules, the number of the reactions (3) and (4) is greater than that of (a), (b) and (c) and the ratio $[\text{H}]/[\text{D}]$ will be determined by them.

$$\frac{[\text{H}]}{[\text{D}]} = \frac{k_3[\text{H}_2] + k_4[\text{HD}]}{k_5[\text{DH}] + k_6[\text{D}_2]} = \frac{1}{\alpha} \quad (5)$$

The total number of atoms will be given of course by reactions (a), (b) and (c), these giving their stationary concentrations:

$$[\text{H}] = \left\{ \frac{k_{ds}[\text{H}_2] + k_{d\alpha}[\text{D}_2] + k_{da}[\text{HD}]}{k_{rs} + k_{r\alpha}\alpha + k_{ra}\alpha} \right\}^{\frac{1}{2}} \quad (6)$$

Now we assume that the same fraction of collisions of H + H and D + D and H + D leads to a recombination. This is, of course, only approximately true. Thus $k_{rs} = k_{r\alpha}$. Furthermore $k_{ra} = 2k_{rs}$, since the number of collisions between n atoms H and n atoms D is twice as great as between n atoms H. From the dissociation equilibrium we obtain:

$$\frac{k_{ds}}{k_{rs}} = K_s; \quad \frac{k_{d\alpha}}{k_{r\alpha}} = K_\alpha; \quad \frac{k_{da}}{k_{ra}} = K_a \quad (7)$$

which yields, inserted into (6)

$$[\text{H}] + [\text{D}] = \sqrt{K_s[\text{H}_2] + K_\alpha[\text{D}_2] + 2K_a[\text{HD}]} \quad (8)$$

With the figures for the dissociation constants at $T = 1000^\circ$ we obtain

$$[\text{H}] + [\text{D}] = \sqrt{1 + \frac{1}{1.32^2} \frac{[\text{D}_2]}{[\text{H}_2]} + \frac{2[\text{HD}]}{1.32[\text{H}_2] \sqrt{K}}}$$

where $K = \frac{[\text{HD}]^2}{[\text{H}_2][\text{D}_2]}$. K is approximately 4 for 1000° abs.

The original concentration of H_2 will be denoted by c . Since the concentration of D_2 was in all experiments practically equal to that of H_2 , the momentary concentration are $[HD] = 2cy$, that of

$$[H_2] = [D_2] = c(1 - y)$$

Thus we have finally the following equation :

$$[H] + [D] = \sqrt{K_c} \cdot \sqrt{1 - y} \cdot \sqrt{1 + 0.57 + 1.57 \frac{y}{1 - y}} \approx 1.25 \sqrt{K_c} \quad (9)$$

This means that the total concentration of atoms is hardly changing at all during the reaction. The numerical value for $[H] + [D]$ is the same as hitherto used.² We assume furthermore that the ratio $[H]/[D]$ is always k_3/k_4 as in the beginning of the reaction.

The kinetic equation for the rate of formation of HD is then

$$2c \frac{dy}{dt} = (k_3[D] + k_4[H])c(1 - y) - (k_1[H] + k_2[D])2cy \quad (10)$$

Integrated, this gives

$$y_\infty - y_t = \frac{a}{b} \cdot e^{-bt} \quad (11)$$

where $a = \frac{1}{2}(k_3[D] + k_4[H])$ and $b = (\frac{1}{2}k_3 + k_2)[D] + (\frac{1}{2}k_4 + k_1)[H]$. Introducing the calculated values of $[H]$ and $[D]$ and expressing k_2 and k_1 by k_3 and k_4 and the equilibrium constant² of the reactions (3) and (4) we have

$$a = \frac{1.25 \cdot \sqrt{K_c} k_3 k_4}{k_3 + k_4} \quad (12)$$

$$b = \frac{1.25 \sqrt{K_c}}{k_3 + k_4} \cdot (k_3 k_4 + 0.38 k_3^2 + 0.67 k_4^2) \quad (13)$$

The time of half-change of the reaction is determined by b . According to the experiments² this time of half-change is 1.5 times greater than that of reaction (1) at the same pressure and temperature (in the region 800°-1000°). Thus

$$b = \frac{k_1 \sqrt{K_c} 2c}{1.5} \quad (14)$$

The factor 2 enters under the square root because at the same pressure the concentration of H_2 is twice as great in pure H_2 (as used for reaction (1)) than it is in the mixture used for the reaction (3) and (4).

Hence we have

$$0.75 k_1 = \frac{k_3 k_4 + 0.38 k_3^2 + 0.67 k_4^2}{k_3 + k_4} \quad (15)$$

which is the only equation for k_3 and k_4 derivable under the above mentioned approximations from the present experiments. Into this equation we shall insert the theoretically calculated values of k_3 and k_4 and see whether it checks.

According to the usual collision number theory, the rate of reaction should vary with the temperature

$$k = 6.06 \cdot 10^{30} \left(\frac{d_a + d_m}{2} \right)^2 \sqrt{\frac{8RT(M_a + M_m)}{\pi M_a M_m}} \cdot S \cdot e^{-W/RT} \quad (16)$$

Here d_a and d_m are the diameters of the colliding particles (atom and molecule), M_a and M_m their masses. S is a steric factor, W the heat of activation. For reaction (1) in the temperature region 873°-1023° abs.

one obtains for $W = 5500$ cal., $S = 0.07$. In the low temperature region the figures are $W = 7000$ cal., $S = 0.13$. Although this is not very unsatisfactory it is obvious that the formula, using rather crude assumptions of the kinetic theory of gases and containing two arbitrary constants S and W , cannot represent the true state of affairs, since a *strict calculation of the reaction velocity constant must be based on the general methods of statistical mechanics.*

2.

A real theory of reaction rates should contain no arbitrary constant at all. Attempts in this direction were made in the following way. London⁸ first introduced the idea of the energy surface. The configuration of a set of atoms (the three H's in (1)) can be described by the distances between them. The energy of the atoms in a configuration is thus a function of their distances

$$E = F(r_{12} r_{13} r_{23})$$

from which their motion during the reaction can be determined to a good approximation by classical mechanics. Classical mechanics can be applied because of the comparatively large masses of the nuclei. The equation of motion, e.g., in the x co-ordinate is

$$M \cdot \frac{\partial^2 x}{\partial t^2} = - \frac{\partial E}{\partial x}$$

It should be emphasised that E can be calculated only by quantum mechanics and that it contains the energy which the electrons have if the configuration is characterised by r_{12} , r_{13} , r_{23} . Since this energy *does not depend on the masses of the nuclei, the energy surface is the same for reactions 1 to 4.* Of course there are, according to the different quantum states of the electrons, many such energy surfaces, but here, in case of chemical reactions, we shall be concerned with the lowest one only.

In Fig. 1 which is taken from the work of Eyring and Polanyi⁹ the contour lines of the energy surface of three H atoms are plotted for a straight configuration $r_{13} = r_{12} + r_{23}$, atom 2 being in the middle. *The angle between the axes r_{12} and r_{23} is chosen in such a way that the free motion (motion under the influence of the gravity) of a small heavy ball on the surface of Fig. 1 corresponds to the motion of the atoms in a straight line.*¹⁰ The valley on the right of the figure corresponds to a molecule formed by the atoms 2 and 3 (r_{23} small) 1 being free. The valley towards the top of the figure corresponds to the molecule formed by the atoms 1 and 2, 3 being free. If the system performs the reaction



the point representing the state of the system must go somehow from the top valley to the valley in the right. The dotted line represents one such path. The following is the picture given by London for exchange reactions.

⁸ London, *Sommerfeld Festschrift*, S. Hirzel, 1928, p. 104.

⁹ Eyring and Polanyi, *Z. physik. Chem.*, 1931, 12B, 279.

¹⁰ Professor O. K. Rice has kindly pointed out that this angle is 60° for three equal masses, instead of 120° , since the sign in formula (25) *Z. physik. Chem.*, 1931, 12B, 279 is incorrect.

The energy of the system is the energy of the heavy ball and it is evident that for very low energies a passage from one valley into the other is impossible. Only if the energy of the system exceeds a certain limit—that of point x in our figure—is such a passage possible. *Points x are the highest points of that path leading from one valley into the other, for which the highest point is as low as possible.* Generally this path has only one highest point—its energy is the activation energy—only in our symmetrical example there are two equally high points. The system in the activation point is called the “activated complex” or simply “complex.” It is evident therefore that the activation energy is given, if the energy surface is known, and this was aimed at in the pioneer work of Eyring and Polanyi.⁹ It should be emphasised, however, that the present more accurate experimental data make more exact calculations desirable. Of course Fig. 1 represents, as already mentioned, the energy surface only for the straight configurations. For all configurations a three-dimensional surface would be necessary, but nothing would be changed fundamentally.

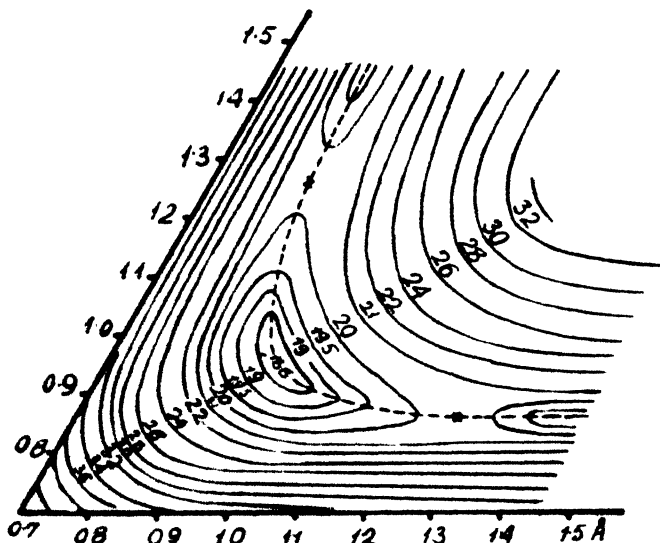


FIG. 1.

If we consider a system of three atoms in a finite box, the energy surface must be cut off at a certain point corresponding to the size of the box. The ball on our energy surface would roll around for some time in one valley, would pass over into the other, etc. The number of passages per unit time is equal to the number of atomic interchanges.

It is not easy to calculate this number exactly. It is quite possible, however, as we shall see, to calculate the number of passages over the lines through the activation points x , where the energy surface forms a saddle. Now, in our case not every passage over a saddle will lead to an atomic interchange. After every passage through one of the saddles the ball will roll around in the little hole of the middle of the figure and after a certain time may go on into the second valley or else may return to the initial one. The relative probability of the first event will be the ratio of the number of atomic interchanges to the number of passages through the saddle.

Although the number of passages through the saddles will be

calculated sufficiently accurately this ratio can be estimated only. It is evidently rather near to $\frac{1}{2}$ in case the atoms 2 and 3 are equal, because the ball in the hole will go out in both directions with equal probability. If the atoms 2 and 3 are different (one D, the other H), though the potential surface is unaltered by this fact, the passage through both the barriers is for some quantum theoretical reasons not equally probable over the two saddles. We shall return to this point later. In this case the number of atomic interchanges will be only slightly smaller than the number of passages over the saddle which is more difficult to cross.

3.

The calculation of the number of passages through a given saddle can be performed by the so-called transition state method.¹¹ *A small strip in phase space is considered perpendicular to the direction of the ball's motion during the reaction. The probability of the ball being in this strip can be calculated by ordinary statistical mechanics. In the classical theory this probability is given by*

$$\eta = \frac{\int_{\text{strip}} ds e^{-V/kT}}{\int_{\text{vol.}} d\tau e^{-V/kT}}$$

In the numerator the integration must be extended over the strip, in the denominator over the whole phase space, V is the (potential) energy. The number of passages is obtained by multiplying this quantity by the mean component of the velocity of the ball which is perpendicular to the strip, and dividing by the width of the strip.

This classical theory must be corrected, of course, for quantum effects. There is the zero point energy, the quantum-mechanical leakage through the barriers and finally the jump from one energy surface to the other, which must be taken into account.

The formula which takes the first two effects into account* and is valid for exchange reactions in which the activated complex is straight is:

$$k = \gamma \frac{1}{2} \left(\frac{M_a + M_m}{M_a M_m} \right)^{3/2} \frac{I_c}{I_m} \cdot \left(\frac{h}{2\pi} \right)^2 \cdot \sqrt{\frac{2\pi}{kT}} \cdot e^{-Q/RT} \cdot \frac{N_L}{1000} \\ \times \frac{\sinh \beta \nu_m}{(\sinh \beta \nu_a)^2 \sinh \beta \nu_s} \cdot (1 + \frac{1}{2} \beta^2 \nu_s^2) \quad (17)$$

Here, M_a and M_m are the masses of the colliding atom and molecule respectively. I_c is the moment of inertia of the activated complex, I_m that of the molecule, Q the activation energy, N_L the Avogadro number, $\beta = \frac{h}{2kT}$, ν_m is the vibrational frequency of the molecule which corresponds to 12 500 cal./mole energy in H_2 and 8900 cal./mole in D_2 ,

¹¹ For the history of this method, cf. Evans and Polanyi, *Trans. Faraday Soc.* 1935, 31, 875.

* This formula is identical with that derived by Pelzer and Wigner³ and Wigner,⁴ and is practically identical with that of Eyring.⁵ Eyring's formula, however, does not contain the zero point energy of the complex explicitly and also neglects the leakage through the barrier.

ν_d is the deformational frequency of the complex and ν_i the other stable frequency of the complex, whereas ν_i is the imaginary frequency of the same: ν_i can be calculated from the curvature of the potential surface in the same way as the real frequencies, except that the second derivative of the potential surface which is negative in this direction must be taken with the positive sign. k is the reaction velocity constant in mole/litre sec.; γ is the above discussed ratio of the number of atomic interchanges to the number of passages through one of the saddles.

The first line of formula (17) takes into account the classical quantities only, the second one contains the effect of the zero point energy of both the molecule and the complex and the effect of quantized vibrational levels. In

$$\frac{1}{2\sinh \beta \nu} = \frac{e^{-\beta \hbar \nu / 2}}{1 - e^{-\beta \hbar \nu}}$$

the numerator is due to the zero point energy $\frac{1}{2}\hbar\nu$, the denominator is the sum of states for the vibrational states.* The last factor $(1 + \frac{1}{2}\beta^2 \nu_i^2)$ contains the "tunnel" effect. In consequence of the negative curvature of the energy surface perpendicular to the strip, some passages will occur by leakage even if the energy of the ball is not high enough to reach the activation point. This manifests itself in the last factor virtually as a negative zero point energy of the activated complex, as it facilitates the reaction.

The deformation frequency is doubly degenerate and ν_d enters as a squared term into (17). A straight 3 atomic molecule has 4 vibrational ($\nu_d, \nu_d, \nu_s, \nu_s$) 2 rotational and 3 translational degrees of freedom, altogether 9 degrees of freedom.

If the energy surface of § 2 is known all quantities entering into (17) may be calculated, thus (17) differs considerably from the formula of kinetic theory. The activation energy Q is the difference between the potential energy of the activation point and the bottom of the valley from which the reaction starts (without zero point energies).

For the calculation of vibrational frequencies, the potential energy in the neighbourhood of the activation point must be known up to the second power terms of the distances. This will be assumed to have the form:

$$\begin{aligned} V &= Q + p(r_{23} - 0.85)^2 - q(r_{12} - 1.25)^2 + s\delta^2 \\ &= Q + p\xi^2 - q\eta^2 + s\delta^2 \end{aligned} \quad (18)$$

the activation point having the co-ordinates $r_{23} = 0.85 \text{ \AA}$, $r_{12} = 1.23 \text{ \AA}$, δ is the deformation angle 123. The fact that no $(r_{12} - 1.25)(r_{23} - 0.85)$ term enters is not evident, *a priori*; but can be seen from the figure, p, q, s are positive constants the values of which can be derived from the Fig. 1.

For the vibrations,¹² ν_i and ν_s , $\delta = 0$ can be assumed and the molecule put into the x -axis. The kinetic energy can be written then if we denote by M_1, M_2 and M_3 the masses of the three atoms

$$\begin{aligned} K &= \frac{1}{2}(M_1\dot{x}_1^2 + M_2\dot{x}_2^2 + M_3\dot{x}_3^2) = \frac{M_1\dot{x}_1 + M_2\dot{x}_2 + M_3\dot{x}_3}{2(M_1 + M_2 + M_3)} \\ &+ \frac{M_1(M_2 + M_3)(\dot{x}_2 - \dot{x}_1)^2}{2(M_1 + M_2 + M_3)} + \frac{M_2(M_1 + M_3)(\dot{x}_3 - \dot{x}_2)^2}{2(M_1 + M_2 + M_3)} \\ &+ \frac{M_1M_3(\dot{x}_3 - \dot{x}_1)(\dot{x}_2 - \dot{x}_1)}{M_1 + M_2 + M_3} \end{aligned} \quad (19)$$

* The vibrational states are considered as "harmonic."

¹² Cross and Vleck, *J. Chemical Physics*, 1933, 1, 350.

which gives, if one omits the first term, assuming that the centre of mass is at rest :

$$K = \frac{M_3(M_1 + M_2)}{2(M_1 + M_2 + M_3)}\dot{\eta}^2 + \frac{M_1(M_2 + M_3)}{2(M_1 + M_2 + M_3)}\dot{\xi}^2 + \frac{M_1M_2\dot{\xi}\dot{\eta}}{M_1 + M_2 + M_3} \\ = \mu_1\dot{\xi}^2 + \frac{1}{2}\mu_2\dot{\eta}^2 + \mu\dot{\xi}\dot{\eta} \quad (20)$$

If the last term were not present, the motion of the ball could be described in rectangular co-ordinates.

The equations of motion are hence $\frac{d}{dt} \cdot \frac{\partial K}{\partial \dot{\xi}} = - \frac{\partial V}{\partial \xi}$, etc.

$$\mu_1\ddot{\xi} + \mu\ddot{\eta} = -2p\xi \quad (21) \\ \mu\ddot{\xi} + \mu_2\ddot{\eta} = +2q\eta$$

Assuming

$$\xi = a^2 \cos 2\pi\nu t, \quad \eta = b^2 \cos 2\pi\nu t$$

we obtain :

$$4\pi^2\nu^2 = \frac{p\mu_2 - q\mu_1 \pm \sqrt{(q\mu_1 - p\mu_2)^2 + 4qp(\mu_1\mu_2 - \mu^2)}}{(\mu_1\mu_2 - \mu^2)} \quad (22)$$

One of the two values of $4\pi^2\nu^2$ is positive, corresponding to the stable vibration ν_s , the other negative corresponding to the unstable vibration ν_u .

The values for p and q can be estimated from the Fig. 2 which shows the two cross-sections of the saddle, $p = 3 \cdot 10^6$ cal./mole \AA^2 , $q = 4 \cdot 10^4$ cal./mole \AA^2 . For the reaction (1) this value of p and q gives $\frac{1}{2}h\nu_s = 5300$ cal./mole, $\frac{1}{2}h\nu_u = 1840$ cal./mole. There is no objection on theoretical grounds against the first figure. A glance at Fig. 2*b* shows, however, that a negative zero point energy of 1840 cal. is not possible in this case, since the energy—distance curve of Fig. 2 does not continue to be even nearly parabolic thus far. We have arbitrarily decreased $\frac{1}{2}h\nu_u$ to 1000 cal./mole in the low temperature region. It should be mentioned that it is not possible to justify this procedure at present, but it hardly affects our results. Eckart¹³ has shown how to calculate the non-classical penetration of potential barriers of rather different shapes and Bell¹⁴ has

used his results for the reaction $\text{H} + \text{H}_2$. It must be mentioned, however, that Eckart's results apply to a one-dimensional problem only and the fact that Bell omitted to take the zero point energy $\frac{1}{2}h\nu_s$ of the perpendicular vibration into account

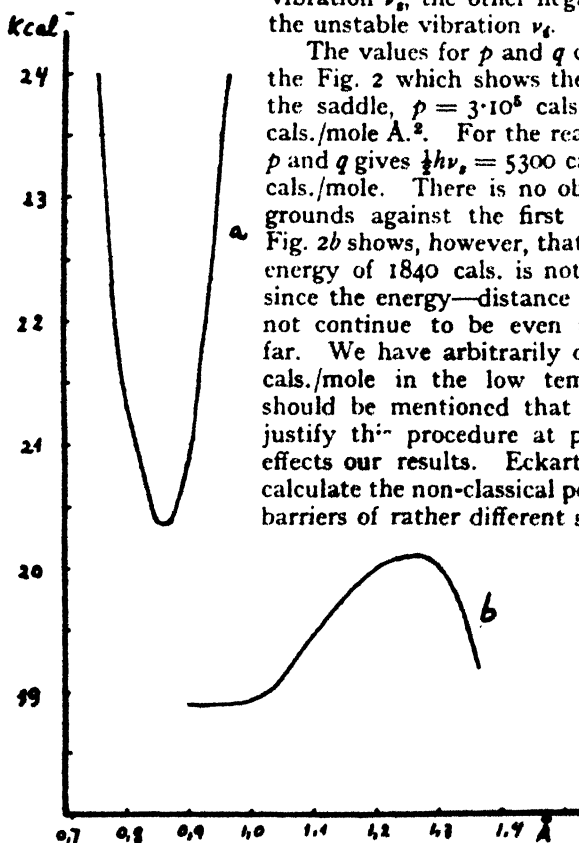


FIG. 2.

¹³ Eckart, *Physic. Rev.*, 1930, **35**, 1303.

¹⁴ Bell, *Proc. Roy. Soc.*, 1933, **139A**, 466.

invalidates his results to some extent. On the other hand the method for many dimensional barriers⁸ is applicable only if the $\frac{h\nu}{kT}$ are not great, i.e., in the high temperature region only. Here (17) has been used consequently, with $\frac{1}{2}h\nu_d = 1840$ cal./mole. Since the formula, though not sensitive for $h\nu_d$, the tunnel effect being always comparatively small, is rather sensitive for $\frac{1}{2}h\nu_s$, the latter *has been determined from the measurements* (cf. section 4) and p calculated backwards. From this new p the $\frac{1}{2}h\nu_s$ were obtained for the other reactions since the ratios of $h\nu_s$ and $h\nu_d$ are practically independent of the value of p . These ratios, as obtained with aid of formula (22), are listed in Table II.

While the displacements are in the direction of the internuclear line for the vibrations ν_s and ν_d , they are perpendicular to this in the deformation vibration ν_d . We shall denote these displacements by y_1, y_2, y_3 for the atoms 1, 2 and 3, the condition that the centre of gravity is at rest and $y = 0$, is then

$$M_1 y_1 + M_2 y_2 + M_3 y_3 = 0 \quad (23)$$

We can put down the condition, furthermore, that the molecule has no angular momentum around the middle atom (in virtue of the previous equation this holds, then around any point):

$$M_1 y_1 \cdot 1.25 - M_3 y_3 \cdot 0.85 = 0 \quad (24)$$

The deformation angle δ is

$$\delta = \frac{y_1 - y_2}{1.25} + \frac{y_3 - y_2}{0.85}$$

and the potential energy $s\delta^2$. The equations of motion are:

$$M_1 \ddot{y}_1 = - \frac{\partial V}{\partial y_1} = - \frac{2s\delta}{1.25}$$

and similar equations for y_2 and y_3 , which are automatically fulfilled, however, if we assume (23) and (24) from the beginning. These equations allow us to express y_3 and y_2 by y_1 and thus δ by y_1 alone. The equation of motion one obtains thus, is:

$$\ddot{y}_1 = \alpha y_1 \quad (25a)$$

$$\alpha = 2s \cdot \left[\frac{1}{1.25^2 M_1} + \frac{1}{0.85^2 M_3} + \left(\frac{1}{1.25} + \frac{1}{0.85} \right)^2 \frac{1}{M_2} \right] \quad (25b)$$

the deformation frequency is consequently

$$\nu_d = \frac{1}{2\pi} \sqrt{\alpha} \quad (26)$$

The constant s should have, according to the calculated energy surface, the value 9000 cal./mole. This gives $h\nu_d = 2150$ cal./mole for reaction (1). It should be mentioned, however, that the value of s is rather sensitive to small changes of the constants from which the energy surface is derived, and not too much stress should be laid on this value of $h\nu_d$.

The ratios of ν_d for the different complexes are listed also in Table II. in which the symbol means (e.g., D—DH) the activated complex of reaction (4) in which the H is nearer to the central D atom than the other D.

This completes the calculation of the frequencies. The ratio of the frequencies for reactions (1) and (2) is always $\sqrt{2}$, independent of the actual model assumed.

TABLE II.

Symbol.	Relative.			I_c .
	ν_s .	ν_t .	ν_d .	
H—HH . . .	5.4	1.77	2.43	3.71×10^{-40}
D—DD . . .	3.8	1.25	1.72	7.42×10^{-40}
D—HH . . .	5.4	1.42	2.37	5.25×10^{-40}
DH—H . . .	4.6	1.38	2.30	4.90×10^{-40}
H—DD . . .	3.8	1.60	1.81	4.90×10^{-40}
HD—D . . .	4.7	1.30	1.91	5.52×10^{-40}

The moment of inertia of the complex I_c which is necessary to calculate the velocity constant according to formula (17) can also be readily obtained from the energy surface. As already mentioned the distances of the end atoms from the central atom are 0.85 Å. and 1.25 Å. In the symmetric case there is only one momentum of inertia, in the asymmetric ones, the momentum of inertia of the complex is different in the two activation points.

If x is the distance of the centre of gravity from the middle atom, the momentum of inertia is given by

$$I_c = M_1(1.25 - x)^2 + M_2x^2 + M_3(0.85 + x)^2$$

and

$$x = \frac{M_1 1.25 - M_3 0.85}{M_1 + M_2 + M_3} \quad (27)$$

I_c does not depend very much on the dimension of the complex. The moment of inertia of the H_2 molecule is known from spectroscopical data. It is 0.467×10^{-40} g. cm.² and is twice as great for D_2 .

4.

In fact the energy surface for reactions 1 to 4 is not known at present with sufficient accuracy, especially not for the calculation of the constants for which (7) is sensitive, i.e., Q , ν_s and ν_d . Therefore another procedure will be adopted in this section: a part of the experimental data will be used to calculate the constants of the energy surface relevant for these quantities.

First of all we shall compare the reaction rates of (1) and (2) in the high temperature region. This ratio is, according to Table I, 1.65 at 950° abs. and we obtain the following equation:

$$\frac{k_1}{k_2} = 1.95 = 2^{3/2} \frac{\sinh 3.29}{\sinh 2.34} \cdot \left(\frac{\sinh \beta \nu_d / \sqrt{2}}{\sinh \beta \nu_s} \right)^2 \frac{\sinh \beta \nu_s / \sqrt{2}}{\sinh \beta \nu_s} \frac{(1 + \frac{1}{2}(3700\beta)^2)^*}{(1 + \frac{1}{2}(3700\beta)^2)} \quad (28)$$

* This formula for the ratio of the velocity constants of the two isotopic reactions is essentially the same—if we neglect the tunnel effect—as the usual one, derived from the kinetic expression (16).

The difference in the "over all" activation energy of the two isotopic reactions is at low temperatures $0.15(h\nu_m - h\nu_s - 2h\nu_d)$.

[Continuation of footnote on next page.]

if ν_d and ν_s are the constants of the complex HHH and 3700 cal., according to the calculation on page 715, ν_s for HHH. Since $\beta\nu_d$ is certainly not greater than unity, we can put $\sinh x = x + \frac{x^3}{6}$ and thus we obtain finally :

$$\frac{\sinh \beta\nu_s/\sqrt{2}}{\sinh \beta\nu_s} = 0.54$$

which gives $\beta\nu_s = 1.9$ and $h\nu_s = 7200$ cal./mole.

In order to calculate the energy of the activation point Q we shall use the experimental figures for the temperature dependence of k_1 . From the figures of the Table I. yields

$$Tw_{\text{exp.}} = T \frac{d \ln k_1}{dT} = 3.4 \text{ to } 3.5 \quad (29)$$

whereas theoretically we obtain for the expression $T \frac{d \ln k_1}{dT}$ from equation (17)

$$T \frac{d \ln k_1}{dT} = -\frac{1}{2} + \frac{Q}{RT} - \beta\nu_m \coth \beta\nu_m + 2\beta\nu_d \coth \beta\nu_d + \beta\nu_s \coth \beta\nu_s - \frac{\beta^2\nu_s^2}{3(1 + \frac{1}{6}\beta^2\nu_s^2)} \quad (30)$$

Inserting the values for ν_m , ν_s and ν_d and putting $2\beta\nu_d \coth \beta\nu_d$ approximately * 2.20 we obtain by comparison with the experimental value for

$$Q/RT = 3.4 \text{ and } Q = 6400 \text{ cal.}$$

According to this calculation the energy of the activation point is rather low and is not in good agreement with the calculated value⁹ which is 20,000 cal. However the first approximation calculations of chemical bonds are generally uncertain by this amount. The remaining unknown frequency ν_d will be determined from the absolute value of the reaction rate of (1) at 950° abs.

$$1.85 \times 10^9 = \frac{2.4 \times 10^{11}}{30.8} e^{-\frac{6400}{RT}} \cdot \frac{\sinh 3.29}{\sinh 1.90} \cdot \frac{1.16}{(\sinh \beta\nu_d)^2} \quad (31)$$

This equation solved yields $\beta\nu_d = 0.74$ and thus $h\nu_d = 2800$ cal./mole.

In the ratio of the two velocity constants the factor

$$= \frac{\sinh \beta\nu_m}{\sinh \beta\nu_m/\sqrt{2}} \cdot \frac{\sinh \beta\nu_s/\sqrt{2}}{\sinh \beta\nu_s} \cdot \left(\frac{\sinh \beta\nu_d/\sqrt{2}}{\sinh \beta\nu_d} \right)^2$$

tends at low temperatures to $e^{(h\nu_m - h\nu_s - 2h\nu_d) \left(1 - \frac{1}{\sqrt{2}}\right) \frac{1}{2RT}}$.

The factor $2^{3/2}$ in the ratio $\frac{k_1}{k_2}$ is partially compensated by the term

$$\left(\frac{\sinh \beta\nu_s/\sqrt{2}}{\sinh \beta\nu_s} \right)^2$$

and becomes (at high temperatures) $\sqrt{2}$. In the kinetic formula this $\sqrt{2}$ arises from the lower number of collisions in the heavier isotope.

* For small $\beta\nu_d$, $2\beta\nu_d \coth \beta\nu_d \approx 2$.

5.

In this section we shall compare the theoretically calculated values for k_3 and k_4 with the experiments and calculate the reaction rates of (1) and (2) at low temperatures. In the case of $H + H_2 \rightleftharpoons H_3 + H$ the theoretical figures can be checked also by the experiments.

k_3 and k_4 can be estimated on basis of the values of Q , $\nu_1\nu_2$ and ν_3 obtained in the preceding sections with aid of the Table II. In these cases, however, the molecular constants of the complexes in the two activation points are not equal, and consequently also the number of passages over the two saddles will be different. The number of passages over the two saddles of the reaction (3) is given by

$$(D - HH) : n_3' = 3.6 \times 10^8 \left(\frac{4}{2.2}\right)^{3/2} 11.25 \frac{\sinh 12400\beta(1 + \frac{1}{2}2960^2\beta^2)}{(\sinh 2730\beta)^2 \sinh 7200\beta} \quad (32)$$

$$(DH - H) : n_3'' = 3.6 \times 10^8 \left(\frac{4}{2.2}\right)^{3/2} 10.50 \frac{\sinh 12400\beta(1 + \frac{1}{2}2880^2\beta^2)}{(\sinh 2750\beta)^2 \sinh 6140\beta} \quad (33)$$

which yields for $n_3' = 2.95 \times 10^9 \frac{\text{mole}}{\text{litre sec.}}$

and for

$$n_3'' = 3.5 \times 10^9 \frac{\text{mole}}{\text{litre sec.}} \text{ at } 950^\circ \text{ abs.}$$

Analogous formula for the reaction $H + D_2$ gives for the saddle (H - DD)

$$n_4' = 2.0 \times 10^9 \frac{\text{mole}}{\text{litre sec.}},$$

and for the saddle (HD - D)

$$n_4'' = 1.7 \times 10^9 \frac{\text{mole}}{\text{litre sec.}}$$

at the same temperature.

The number of atomic interchanges which in the symmetric cases was calculated with $\gamma = \frac{1}{2}$ from the number of passages over one of the saddles, in the case of the reactions (3) and (4) can only be estimated. Since for $n' = n''$ $\gamma = \frac{1}{2}$, and for the other limiting case if $n' > n''$ with $\gamma = 1$, $k = n''$, we shall put in both cases $\gamma = \frac{2}{3}$, and thus k_3 and k_4 become

$$k_3 = 2.2 \times 10^9 \frac{\text{mole}}{\text{litre sec.}}$$

$$k_4 = 1.27 \times 10^9 \frac{\text{mole}}{\text{litre sec.}}$$

In order to compare these theoretical values for k_3 and k_4 with the experiments we have to insert them into the formula (15) of section 1. The right side of the formula yields 1.65×10^9 in agreement with the experimental value 1.4×10^9 . The agreement must be considered quite good, especially since the right side of the formula (15) is proportional to γ , which was chosen rather arbitrarily $\frac{2}{3}$. Unfortunately, lack of more experimental and theoretical data about the reactions (3) and (4) makes it impossible for us at present further to check formula (15) for a wide range of H_2 and D_2 concentrations, and also for different temperatures.

It is remarkable that the velocity of reaction (3) is the fastest among all elementary reactions of hydrogen. This is caused by the comparatively low zero point energy of the activated complexes $D-HH$ and $DH-H$. This was predicted by Polanyi¹⁵ on qualitative considerations.

In Fig. 3 the energy diagrams for all the reactions (1 to 4) are sketched.

In the initial state the zero point energy difference of H and D is neglected (the zero point energy difference of H and D is 84 cal., H having with this amount greater ionisation energy), in the activated state only the positive part of the zero point energy is taken into account. Qualitatively the energy levels of the complexes are in the same order like those which, in the paper of Farkas and Farkas were calculated on basis of rather crude assumptions about the force constants of the activated complexes. The main difference in the absolute values of the zero point energies arises from the inclusion of the deformation frequencies which were neglected in *cf.* 2.

Much less satisfactory is the agreement between the theoretically calculated rates for the reaction (1) and the experimental figures at low temperatures, as given in Table I. For the reaction (2) thus far no experimental data are known at low temperatures.*

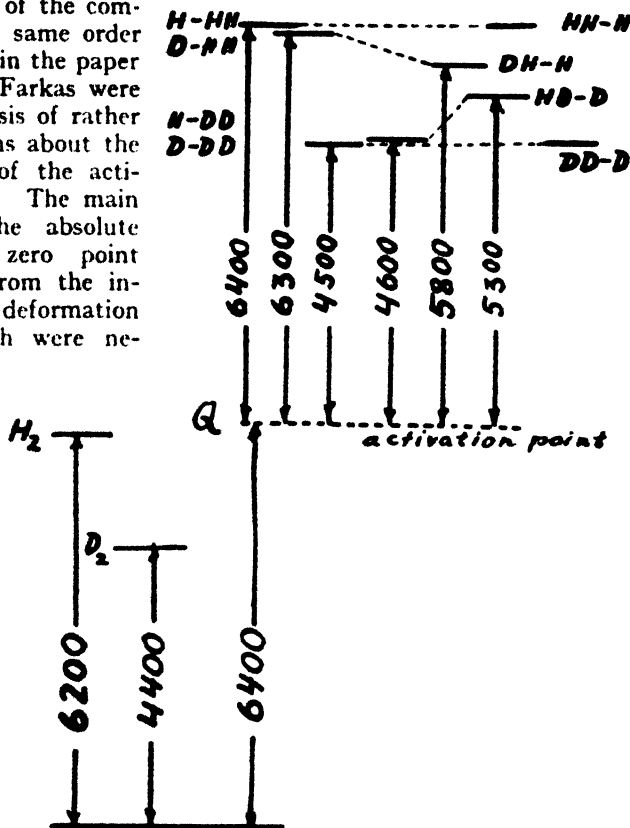


FIG. 3.

With the con-

stants, Q , ν_a , ν_d obtained in section 4 and ν_t which was derived from the rough energy surface, the calculation of the rates of the reaction (1) is as follows:

The tunnel effect in this region as mentioned on page 715 is sufficiently accurately given by $(1 + 1/6(2000\beta)^2)$ which factor has at $T = 283^\circ$ abs. the value 1.52 and, at $T = 373^\circ$, 1.30. At this temperature region $\sinh x$ can be replaced by $\frac{1}{2}e^x$ and we obtain, inserting the numerical values into (17),

¹⁵ Polanyi, *Nature*, 1934, 133, 26.

* According to the theoretical formula (17) the ratio of k_1/k_2 should at room temperature be 3.1.

$$5.7 \times 10^{10} \times 1.52e^{-\frac{6600}{283 RT}} = 6.9 \times 10^5 \frac{\text{mole}}{\text{litre sec.}},$$

$$5.0 \times 10^{10} \times 1.30e^{-\frac{6600}{373 RT}} = 8.8 \times 10^6 \frac{\text{mole}}{\text{litre sec.}},$$

instead of the experimental figures of $1.3 \times 10^5 \frac{\text{mole}}{\text{litre sec.}}$ and $3.1 \times 10^6 \frac{\text{mole}}{\text{litre sec.}}$ at the corresponding temperatures.

The 6600 Cal. which appears in the exponential factor is the "over all" activation energy at low temperatures. This energy W is in this region

$$W = Q - \frac{1}{2}h\nu_m + h\nu_d + \frac{1}{2}h\nu_s.$$

Theoretically, k_1 is thus given by :

$$k_1 = 6.06 \times 10^{20} \times \left(\frac{M_a + M_m}{M_a M_m} \right)^{3/2} \frac{I_c}{I_m} \frac{h^2}{\sqrt{2\pi k}} T^{-1/2} e^{-\frac{W}{RT}} \left(1 - \frac{1}{6} \left(\frac{500}{T} \right)^2 \right)^* \quad (34)$$

T enters into this formula, besides the exponential factor essentially in the $-\frac{1}{2}$ power, in contrast to the kinetic formula, and also to the theoretical temperature dependence at high temperatures.

It is at present impossible to tell whether this discrepancy is caused by some errors in the experiments or by the imperfection of the theory. It must be emphasised, however, that it is impossible to fit both the low and the high temperature measurement on the reaction rate of (1) to the theoretical calculations by alteration of the constants ν_s , Q , ν_d of section 4.

If one uses the low temperature measurements, instead of the temperature dependence of k_1 at high temperatures, to determine the vibrational frequencies, one obtains the following set of values: $h\nu_s = 10600$ cal./mole, $h\nu_d = 1500$ cal./mole and the activation energy becomes 7800 cal./mole. With these constants one can fit all measurements, except, however, the temperature dependence of k_1 and k_2 in the high temperature region.

Possibly the calculation of Q from the temperature dependence of k_1 at high temperatures according to equation (30) is affected with the greatest inaccuracy. The temperature dependence of k_1 is namely derived from the data about the thermal conversion of $p\text{-H}_2 \rightarrow o\text{-H}_2$. The velocity of this reaction varies very much, since the thermal H atom concentration is enormously increased with rising temperature, and thus the directly measured figures on the temperature dependence of the reaction $p\text{-H}_2 \rightarrow o\text{-H}_2$ show a more than ten times higher temperature coefficient than that of k_1 itself. In k_1 , for instance, the increase of the thermal H atom concentration has been taken already into account. In this connection it should be mentioned that the experimental figure for $\frac{Td \ln k_1}{dT}$ is practically the same as for reaction (1), namely 3.5, whereas

* By dividing this formula by the kinetic formula (16) (if we neglect the tunnel effect) we obtain for the steric factor the complicated expression

$$S = \frac{M_a + M_m}{M_a M_m} \times \frac{I_c}{I_m} \times \frac{h^2}{(d_s + d_m)^2 2\pi k T}$$

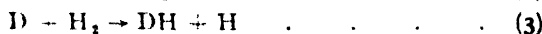
Hence S is, in the low temperature region, proportional to T^{-1} .

according to the formula (30) the theoretical value with the respective values for the molecular-constants of the complex DDD yields 4.12. This discrepancy may be due to the state of affairs just mentioned, which holds also for reaction (2). A small uncertainty in the larger temperature coefficients of the thermal *ortho-para*-conversions causes a comparatively large uncertainty in the temperature dependence of reactions (1) and (2).

If we assume that the measurements at high temperatures on the reactions (1) and (2) are fairly correct, the discrepancy at low temperature between the experimental data and the theoretical rate must be ascribed, as already mentioned, either to errors in the experiments or to some imperfection of the theoretical treatment. It is planned to revise the experimental data in a wide temperature range for both reactions, since it seems very important to decide whether the present theory of reaction velocities, as developed recently, is correct or not.

Summary.

The velocity constants of the elementary reactions of hydrogen and deuterium



are calculated on basis of the formula

$$k = \gamma \frac{1}{2} \times \left(\frac{M_a + M_m}{M_a M_m} \right)^{1/2} \frac{I_e}{I_m} \times \left(\frac{h}{2\pi} \right)^2 \sqrt{\frac{2\pi}{hT}} \times e^{-Q/RT} \frac{N_L}{1000} \\ \times \frac{\sinh \beta \nu_m}{(\sinh \beta \nu_d)^2 \sinh \beta \nu_s} \cdot (1 + \frac{1}{2} \beta^2 \nu_s^2)$$

which was derived by Pelzer and Wigner and Wigner for this type of reaction. The constants ν_m and I_m of the molecule are known from spectroscopic data. The molecular constants I_e , ν_s , ν_d for the different complexes involved in reactions (1 to 4) are partly computed by the energy surface of these reactions and partly obtained by comparison of one part of the experimental data with the theory. The remaining experimental data on reactions (1 to 4) are then compared with the calculated velocity constants.

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THE PHOTO-OXIDATION OF METHYLENE IODIDE.

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PART I.

The photo-oxidation of methyl and ethyl iodides has already been investigated and the products obtained interpreted in terms of reactions between the methyl and ethyl radicals and molecular oxygen.¹

The importance of these radicals in the oxidation of organic compounds is, however, probably secondary to that of the methylene radical.² Kassel,³ as a result of his study of the pyrolysis of methane, suggested that this radical was chemically rather inert. More recent work, however, has thrown considerable doubt on the reality of the inertness of methylene and the part played by it in methane pyrolysis.⁴ The investigation of reactions in which there are good grounds for believing that methylene is formed is, therefore, likely to be of considerable value. Norrish⁵ has demonstrated the probable formation of methylene by the photo-decomposition of diazomethane, and the photo-dissociation of gaseous methylene iodide might also be expected to give rise to this radical.

Methylene iodide was chosen for the present work on account of its far greater stability. Parallel experiments with diazomethane were also commenced but discontinued after a number of explosions had been experienced.

Materials.

Commercial methylene iodide was treated with thiosulphate to remove iodine, washed with water and, after drying with calcium chloride, was distilled *in vacuo*.

Oxygen from a cylinder was passed through a liquid air trap and used without further purification.

Apparatus.

Preliminary experiments to discover the nature of the products and the best conditions were carried out in the simplest possible manner. Oxygen stored in an aspirator was sucked by a "Hyvac" pump through a train consisting of a drying tube, capillary, bubbler filled with methylene iodide, a cylindrical silica reaction cell, a second capillary and a liquid air trap. The capillaries were chosen so as to give a pressure of a few cms. of Hg in the cell, which was illuminated with the full light of a mercury arc.

¹ J. R. Bates and R. Spence, *J.A.C.S.*, 1931, **53**, 1689; L. T. Jones and J. R. Bates, *ibid.*, 1934, **56**, 2285.

² R. G. W. Norrish, *Proc. Roy. Soc.*, 1935, **150A**, 36.

³ L. S. Kassel, *J.A.C.S.*, 1932, **54**, 3949.

⁴ F. O. Rice and A. L. Glasebrook, *ibid.*, 1934, **56**, 2381; Belchetz, *Trans. Faraday Soc.*, 1934, **30**, 170.

⁵ F. W. Kirkbride and R. G. W. Norrish, *J.C.S.*, 1933, 119.

The results obtained indicated the probable formation of gaseous products. The low vapour pressure of methylene iodide (about 1 mm. Hg at room temperature) was not favourable to the use of a static system and a closed circulating system was consequently adopted.

The apparatus is shown diagrammatically in Fig. 1.

Two thermostats were employed, one of which contained only the methylene iodide saturator A, consisting of 40 cms. of 2 cm. diameter tubing placed horizontally and about half filled with methylene iodide. From one end of the saturator a tube led directly to the reaction cell, B, which was fixed in front of a quartz window in the second thermostat. The other end of the reaction cell was connected with the traps C, D, E, the manometer F, the flow meter G, and the mercury diffusion pump H, which worked satisfactorily up to pressures of 20 mm. Hg.

Following the pump came a half-litre bulb I, which brought the total volume up to a suitable value and being placed in the second thermostat, helped to nullify the effects of temperature changes on the unthermostated portions of the apparatus. Finally, the bulb was connected through a trap K, to remove mercury vapour, with the other end of the saturator.

Leads were taken to a Hyvac pump and to a Toepler pump, which extracted specimens of the gas for analysis in a Bone and Wheeler apparatus. The manometers F and G were filled with butyl phthalate. Exposed tubing with which methylene iodide came in contact was heated above the condensation temperature electrically.

The effective volume of the apparatus under working conditions was determined by admitting oxygen at atmospheric pressure from the calibrated volume M to the apparatus and measuring the pressure increase on F. The total volume was about 1200 c.c. and the usual rate of circulation about 24 litres per hour.

The light source was an atmospheric quartz mercury arc burning at 2.2 amperes from a regulated 110 volt circuit. Especially in the later experiments the light was rendered approximately parallel with a quartz lens and for some series a 5 mm. layer of potassium chromate (0.5 gm. per litre) was used as a filter.

Two reaction cells were used. The first was a cylindrical bulb 4.5 cm. diameter and volume 150 c.c. with inlet and outlet tubes at opposite ends. It was placed broad-side on to the light beam. The second cell was also cylindrical but fitted with plane parallel end plates. It was 10 cm. long and of volume 220 c.c. Its disposition is shown in Fig. 1. The first cell was attached to the apparatus by ground joints sealed with "Apeizon" wax, the second by graded silica-soda glass seals.

Procedure.

In order to obtain enough of the products for an accurate analysis, each experiment was continued for about three hours or, when low intensities were used, six hours.

A mixture of ice and salt was placed around the trap C and liquid air around the others. Oxygen was then admitted to the desired pressure, and the heating of the circulating pump adjusted to give the correct rate

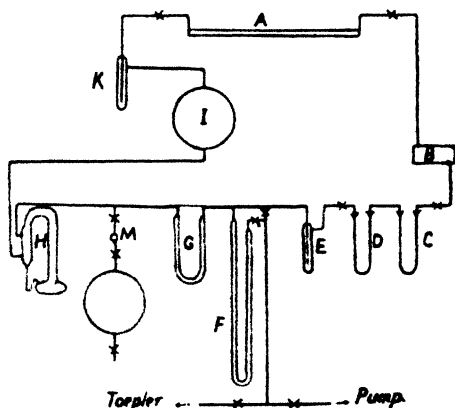


FIG. 1.

of flow. As soon as steady conditions had been obtained, the insolation was commenced.

At the conclusion of the insolation, the traps C and D were isolated and evacuated in order that the entire condensate could be distilled into the trap C, which was made in the form of a U-tube in order to ensure that all of the condensate was removed for analysis.

Meanwhile a portion of the gas was pumped off and analysed for carbon monoxide and hydrogen, which were the only gaseous products which could be detected.

In addition to iodine, the following were shown to be present in the condensate by means of the tests given.

Formaldehyde.—(1) Formation of polymer m.p. 172° , which decomposes to give smell of formaldehyde.

(2) Derivative with 3 : 5 dinitro-phenylhydrazine m.p. 155° .

Formic Acid.—(1) Characteristic test with HgO .

(2) Acidity to methyl orange.

Ethylene Glycol.—(1) Formation of dibenzoate m.p. 71.5° .

(2) Formation of 2:4 dinitrobenzoate which exploded at about the same temperature as a known specimen. Instead of ethylene glycol the products may be ethylene oxide and water. The concentrations available were insufficient to enable this rather minor point to be settled. There was no evidence for any other substances and in particular methyl or ethyl alcohols, which were especially looked for.

For the quantitative analysis of the condensate the following procedure, which was tested out with known mixtures, was adopted :

Free iodine was first titrated with $N/10$ thiosulphate, a more dilute solution being found inadvisable as the accuracy of the formaldehyde estimation was reduced if the volume of the aqueous layer was too large. The formic acid was then titrated with $N/50$ NaOH using methyl orange as indicator, and the formaldehyde then determined by the well-known hydroxylamine method.

For ethylene glycol no satisfactory analytical method could be found,

and recourse had to be had to "element balances." The carbon, hydrogen and oxygen unaccounted for as HCOOH , HCHO , CO or H_2 in a few typical cases is shown in Table I. The data from which they have been calculated are given in Table II.

Although rather irregular, it is clear that the ratios of C : H : O average closely to 1 : 3 : 1, the empirical formula of glycol. It is therefore very improbable that any other substance is formed in appreciable amount.

TABLE I.—MOLS. $\times 10^{-4}$ PER HOUR
UNACCOUNTED FOR.

No.	C	H.	O.	$2(\text{CO}-\text{H}_2)$.
2	0.409	1.240	0.431	0.422
3	0.426	1.352	0.568	0.500
5	0.523	1.602	0.523	0.536
6	0.551	1.668	0.567	0.566
7	0.534	1.652	0.618	0.584
21	0.757	2.180	0.608	0.666
22	0.694	2.074	0.685	0.686
24	0.897	2.580	1.014	0.786
26	0.878	2.638	0.742	0.882

It will be further observed that the last column of Table I. which gives twice the difference between the mols. of carbon monoxide and hydrogen formed is always very near to the unaccounted carbon and oxygen. We have accordingly assumed that carbon monoxide and glycol are formed in the reaction in equimolecular proportions. There then remains unexplained a small quantity (about 10 per cent. of the total) of carbon monoxide and an equivalent quantity of hydrogen. This is almost certainly due to photo dissociation of formaldehyde.

The amount of glycol can therefore be calculated from the difference between the carbon monoxide and hydrogen, or from the carbon or oxygen balances.

Results.

Complete analyses were in general carried out for each run.

The experimental results are given in Table II. The runs up to number 26 were obtained with the "bulb" cell illuminated with the full mercury arc light. For the subsequent runs the cylindrical cell with plane end-plates was used. The light was filtered through potassium chromate solution for runs 37 to 59, but no filter was used for the last runs.

When the oxygen was replaced by hydrogen the amount of iodine formed was barely detectable.

In addition to the results of Table II., a few runs were carried out with oxygen at atmospheric pressure in which the yield of iodine was approximately what would be expected from an extrapolation of the results obtained at the lower pressures. These are not included, since some formaldehyde polymer tended to form in the cell, and their accuracy is therefore suspect.

During the determination of the quantum yield, however, when the intensities were very much lower, no trace of polymer was formed, although the total pressure was also atmospheric.

The pressure drop across the flowmeter capillary was maintained throughout at 25 mm. of butyl phthalate, and in order to interpret the results, it was necessary to convert this pressure difference to the equivalent rate of flow at the various pressures used. The calibration was effected during runs 37 to 59 by weighing the condensate collected in the traps.

If p_m is the pressure recorded by the manometer F (Fig. 1), T_m its temperature, T_s the reaction cell temperature, p_s the vapour pressure of methylene iodide at the saturator temperature, V_s the volume rate of flow of oxygen through the cell, V_m that through the flowmeter, and W is the weight of products collected in unit time, we have :

$$\frac{p_m V_m}{RT_m} = \frac{(p_m - p_s) V_s}{RT_s} = \frac{p_m - p_s}{p_s} \cdot \frac{W}{268}.$$

The flowmeter was unthermostated but the room temperature was constant to within 3° C.

In the above it is assumed that there is no pressure drop between the cell and the manometer. This was tested by adding a second manometer temporarily to the outlet tube of the cell. No appreciable difference in pressure appeared until the total pressure was reduced below 5 mm. At 4 mm. of mercury the difference was 0.2 mm. Hg.

The error introduced by the reaction products is negligible since at the most only 8 per cent. of the methylene iodide reacted and the weight of the oxygen absorbed is partially offset by the formation of carbon monoxide.

Direct diffusion of methylene iodide from the saturator to the traps does not occur under the conditions used, since with the saturator at 35° C. ($p_s = 2.52$ mm.) and a time of 3 hours no detectable amount of methylene iodide collected in the trap until the total pressure was reduced below 4 mm. Hg.

Variation of the intensity produced rather less than a proportional change in the rate of formation of iodine. A screen transmitting 16.8 per cent. of the incident intensity reduced the rate of iodine formation to 24.1 per cent., 22.1 per cent. and 19.5 per cent. when the oxygen pressures were respectively 4.0, 6.1 and 20.0 mm. Hg.

Increasing the rate of flow causes an increase in the rate of iodine formation.

The only data discoverable in the literature ⁶ for the vapour pressure of methylene iodide are two boiling-points, one for atmospheric pressure, 180°

⁶ Beilstein, Vol. I., p. 71.

TABLE II.

1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	13.	14.
No.	Reaction Cell Temp.	V.P. of CH_2I_2	P mm. Hg.	Mols. $\times 10^4$ Formed per Hour.					Mols. $\times 10^4$ O_2 Absorbed per Hour.	k_1/k_2 $\times 10^4$.	k_2/k_1 $\times 10^4$.	α	$\phi\delta E$ $\times 10^4$.
				I_2	HCOOH.	HCHO.	CO.	H_2					
1	35°		4.00	0.892	0.167	—	—	—	—	5.92	—		
2			5.00	1.059	0.167	0.250	0.233	0.022	0.627	4.52	0.71		
3			6.35	1.217	0.175	0.333	0.283	0.033	0.767	4.42	1.14		
4		2.52	8.11	1.405	0.267	0.417	—	—	—	6.16	1.70		
5			10.00	1.583	0.283	0.407	0.300	0.032	0.928	5.72	1.85		
6			11.83	1.750	0.350	0.516	0.333	0.050	1.058	6.58	2.11	152 (?)	4.27
7			14.01	1.817	0.383	0.550	0.350	0.058	1.142	7.02	2.36		
8	30°		3.47	0.774	—	—	—	—	—	—	—		
9			7.01	1.523	0.322	0.458	0.329	0.033	1.013	5.14	2.18		
10			8.84	1.785	0.376	0.460	0.377	0.042	1.133	5.12	2.03		
11		1.82	10.26	1.968	0.400	0.483	0.405	0.048	1.275	4.90	1.85		
12			15.57	2.155	0.411	0.497	0.427	0.045	1.279	4.54	1.80	27.45	2.64
13			19.23	2.220	0.417	—	0.472	0.049	1.350	4.44	—		
14			23.46	2.250	0.419	0.517	—	—	—	4.40	1.81		
20	45°		4.23	1.624	0.243	0.205	—	—	—	3.22	0.72		
21			6.48	1.900	0.343	0.433	0.367	0.034	1.097	4.04	1.47		
22			6.90	1.942	0.349	0.514	0.385	0.042	1.141	4.02	2.00		
23		1.82	7.30	2.073	0.300	0.441	—	—	—	3.86	1.44	14.0	2.62
24			11.90	2.245	0.424	0.479	0.445	0.052	1.293	4.26	1.53		
25			18.35	2.330	0.429	0.514	—	—	—	4.14	1.66		
26			19.23	2.333	0.445	0.518	0.492	0.051	1.373	4.32	1.69		

	20°	0.67						29.2	0.300
37	3.15	0.237	0.0027	0.0894	—	—	0.157	2.64	1.02
38	4.61	0.255	0.0647	—	—	—	—	2.50	—
39	5.38	0.262	0.0686	0.1165	0.0230	—	—	2.60	1.53
40	6.54	0.265	0.0765	0.1180	—	—	—	2.08	1.54
41	7.70	0.274	0.0774	0.1207	0.0250	—	0.182	2.80	1.44
42	9.54	0.282	0.0813	0.1215	0.0271	—	0.182	2.97	1.33
43	10.00	0.281	0.0781	0.1247	—	—	—	2.82	1.41
44	12.30	0.285	0.0778	0.1289	0.0204	—	0.181	2.75	1.42
45	13.50	0.288	0.0822	0.1298	0.0272	—	0.188	2.93	1.46
46	14.00	0.291	0.0796	0.1307	—	—	—	2.70	1.40
47	16.16	0.290	0.0782	0.1310	0.0270	—	0.189	2.71	1.38
48	19.48	0.291	0.0818	0.1315	—	—	0.191	2.94	1.42
49	23.08	0.294	0.0800	0.1323	—	—	0.190	2.81	1.34
50	3.50	0.245	0.0650	0.0932	—	—	0.156	2.57	1.09
51	4.46	0.258	0.0756	0.1023	—	—	—	2.89	1.34
52	5.77	0.269	0.0784	0.1142	—	—	0.178	2.88	1.30
53	7.85	0.279	0.0775	0.1174	0.0270	—	0.178	2.67	1.18
54	8.46	0.281	0.0786	0.1182	—	—	—	2.71	1.18
55	10.30	0.287	0.0784	0.1198	—	—	—	2.62	1.10
56	11.54	0.288	0.0785	0.1251	0.0271	—	0.182	2.62	1.22
57	14.62	0.290	0.0794	0.1281	—	—	0.186	2.63	1.25
58	16.54	0.291	0.0809	0.1297	—	—	—	2.69	1.29
59	20.00	0.294	0.0820	0.1310	—	—	0.190	2.70	1.29
60	5.49	1.271	0.155	0.286	0.284	0.014	0.698	2.63	0.98
70	6.50	1.402	0.177	0.303	0.319	0.015	0.782	2.73	1.00
71	7.89	1.502	0.187	0.307	0.358	0.034	0.847	2.69	0.96
72	8.54	1.510	0.204	0.320	0.359	0.018	0.850	2.95	1.07
73	10.85	1.643	0.210	0.327	0.386	0.020	0.919	2.77	0.99
74	13.22	1.684	0.215	0.339	0.399	0.021	0.937	2.77	1.02
75	15.30	1.763	0.224	0.345	0.421	0.020	0.974	2.75	1.02
76	17.15	1.778	0.226	0.362	0.430	0.021	1.009	2.75	1.10
77	19.70	1.818	0.236	0.363	0.428	0.023	1.037	2.82	1.09
78	21.95	1.830	0.235	0.372	0.432	0.027	1.040	2.79	1.13

with decomposition, and the other 88° at 39 mm. Hg. It was, therefore, necessary to determine the course of the vapour pressure-temperature curve over the range covered by the kinetic measurements.

Vapour Pressure.

Methylene iodide was placed in a flat bulb about 6 cm. in diameter connected with a sensitive "spoon" gauge and evacuated with a Hyvac pump. All parts of the apparatus with which methylene iodide vapour came in contact were immersed in a thermostat. The outside of the spoon gauge was balanced by admission of air, the pressure being measured by a butyl phthalate manometer which was continuously evacuated on one side. The data in Table III. can be represented by the equation :

$$\log_{10} p = 8.566 - \frac{2520}{T}$$

with a maximum error of 8 per cent.

TABLE III.—VAPOUR PRESSURE DATA.

Temp. C.	V.P. mm.	Temp. C.	V.P. mm.	Temp. C.	V.P. mm.
15.0	0.67	28.1	1.53	40.25	3.48
17.2	0.74	29.5	1.90	41.0	3.53
20.6	1.005	32.5	2.19	43.5	4.23
24.7	1.19	34.0	2.40	47.0	4.91
25.6	1.28	37.7	2.90	50.0	5.58
27.2	1.40	39.0	3.14	51.1	5.92
				55.0	7.53

Quantum Yield.

The quantum yield with respect to iodine was determined for light of mean wavelength about 3100 Å. isolated from the mercury arc spectrum by means of a large quartz monochromator. The reaction cell was the same as that used in runs 37 onwards. For the sake of convenience it was decided to use oxygen at atmospheric pressure saturated with methylene iodide at 21° which was about 1 degree lower than the temperature at which the cellar in which this determination was carried out, could be readily maintained.

The light from the exit slit of the monochromator was rendered approximately parallel by a quartz lens before passing through the cell and finally focussed by a second lens onto a Moll surface thermopile. The E.M.F. generated in the thermopile was measured with a Cambridge vernier potentiometer in conjunction with a Kipp and Zonen Zernicke Zc galvanometer. The thermopile was calibrated against a standard lamp supplied by the U.S. Bureau of Standards. Readings of the incident and transmitted intensities were taken at hourly intervals, by first noting the E.M.F. while the gas stream was flowing and then closing a tap between the saturator and the reaction cell and, after evacuating the cell, again taking the potentiometer reading.

The duration of each run was six hours. The readings obtained had to be corrected for the reflection losses at the crystal quartz plate covering the thermopile, the second quartz lens and the back plate of the cell. Those at the plate and lens were calculated as for two plates and that of the back plate of the cell was taken as the square root of the total loss in the cell. Since the total light lost in passing through the cell was rather greater than that calculated for two plates, the cell was reversed for half of the determinations, without, however, causing any detectable change in the observed quantum yield. In order to avoid as far as possible complications due to back reflections from the large number of surfaces in the light path, all

apparatus was tilted a few degrees from the perpendicular to the optical axis.

The values of the quantum yield obtained were 1.47, 1.46, 1.44, 1.45, 1.43, 1.44, giving as the mean 1.45.

According to Henrici¹ the maximum of the extinction coefficient lies at about 3000 Å. No further data was discoverable in the literature. The absorption spectrum of gaseous methylene iodide was accordingly determined photographically using a Spekker photometer.

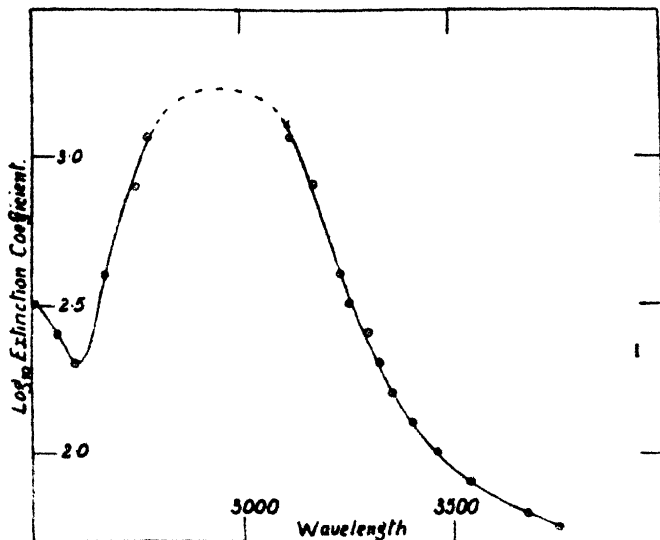
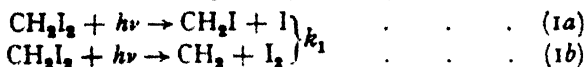


FIG. 2.

The logarithms of the decadic molecular extinction coefficients are plotted against the wavelength in Fig. 2, which also includes one value for 313 mμ obtained by the thermopile-galvanometer method.

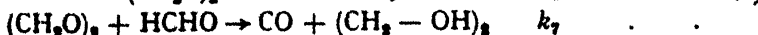
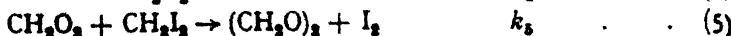
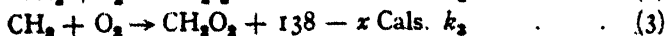
Discussion.

There exist two alternatives for the primary photo process:—

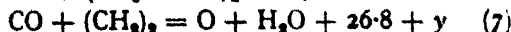


By analogy with other somewhat similar cases we may, however, expect that the remaining iodine atom in CH_2I is very weakly bound so that even with (1a) free methylene may in fact be formed very shortly after the light absorption. The succeeding reactions will be essentially the same with both processes and in the absence of definite data (1b) will be assumed to occur.

Succeeding (1b) the following series of reactions which is the simplest of those we have tried and provides the most satisfactory mechanism, is assumed to occur:—



or



¹ A. Henrici, *Z. Physik*, 1932, 77, 35.

As will be shown in a later paper, the reacting system possesses strong oxidising powers, which we believe to be due to the two molecules, CH_2O_2 and $(\text{CH}_2\text{O})_2$, methylene peroxide and ethylene peroxide.

Reaction 7 was introduced only with considerable diffidence. The equivalence of the carbon monoxide and glycol formed is, however, explained by this reaction so satisfactorily, while no other suitable reaction could be found, that there seems no doubt that, granting the validity of the remaining reactions, this reaction is a real one.

The monomolecularity of reactions (4) and (6) will be discussed later.

Reaction between methylene and methylene iodide to produce ethylene and iodine apparently does not occur since no ethylene could be found among the gaseous products when solid CO_2 was placed around the traps instead of liquid air. The difficulties of detecting a trace of ethylene iodide or ethylidene iodide in the products makes it impossible to decide whether either of these substances is produced.

The gases entering the reaction cell have, during any one run, an almost constant composition deducible from the total pressure recorded by the manometer F, and the temperature of the saturator thermostat. The gases leaving the reaction cell, will shortly after the commencement of the insolation, when steady conditions have been attained, also have a constant composition, which differs from that of the entrant gases, in that the partial pressures of methylene iodide and oxygen are somewhat reduced (CH_2I_2 a maximum of 8 per cent.) and an equivalent amount of the products is present.

Inside the cell itself diffusion and convection will assist in maintaining the composition spacially fairly uniform. As a simplification it will be assumed that the composition throughout the cell equals that of the outflowing gases.

The steady concentration of the short-lived intermediates CH_2 , CH_2O_2 , $(\text{CH}_2\text{O})_2$ should be so low that the amount of them swept away into the traps is negligible compared to that which reacts. On the other hand, the removal of the stable end-products by the gas stream is an important factor determining their concentrations in the cell.

If we represent the concentration in the reaction cell of

by $\begin{matrix} \text{O}_2, & \text{CH}_2\text{I}_2, & \text{CH}_2, & \text{I}_2 & \text{CH}_2\text{O}_2, & \text{HCHO}, & (\text{CH}_2\text{O})_2, & \text{HCOOH}, & \text{and} & (\text{CH}_2\text{OH})_2 \\ X, & Y, & B, & C, & D, & F, & H, & L, & \text{and} & M \end{matrix}$

respectively, and

let E be the Einsteins of light absorbed/hour/litre,

V_0 be the volume rate of flow through the cell in litres/hour,

and ϕ be the volume of the cell,

the rate of formation of iodine in the cell is given by

$$\frac{dc}{dt} = E + k_5 DY - k_2 BC.$$

The condition for a steady iodine concentration in the cell is that the quantity of iodine formed in unit time equals the quantity removed by the gas stream in the same time ;

$$\therefore \phi \frac{dc}{dt} = V_0 C$$

$$\therefore E + k_5 DY - k_2 BC = \frac{V_0 C}{\phi} \quad . \quad . \quad . \quad (8)$$

D, B and H can be evaluated by the usual methods in terms of the

concentrations of the stable substances and on substituting in (8) and simplifying, we get:

$$C = \frac{X}{2d} \left\{ \sqrt{\left(1 + \frac{4\alpha\phi\beta E}{V_0 X}\right)} - 1 \right\}.$$

where

$$\alpha = k_2/k_3 \text{ and } \beta = \frac{2k_5 Y + k_4}{k_5 Y + k_4}$$

The gram mols. of iodine collected in the traps in one hour

$$\begin{aligned} &= V_0 C \\ &= \frac{V_0 X}{2\alpha} \left\{ \sqrt{\left(1 + \frac{4\alpha\phi\beta E}{V_0 X}\right)} - 1 \right\}. \end{aligned}$$

But

$$V_0 X = \frac{V_0(p_m - p_z)}{RT_0} = \frac{V_m p_m}{RT_m}.$$

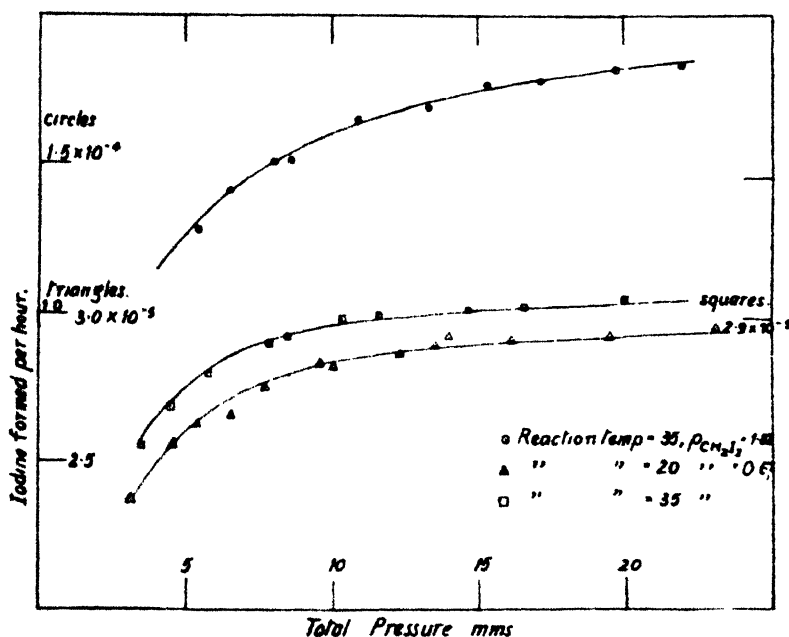


FIG 3.

∴ Iodine collected per hour

$$= \frac{V_m p_m}{2RT_m \alpha} \left\{ \sqrt{\left(1 + \frac{4RT_m \alpha \phi \beta E}{V_m p_m}\right)} - 1 \right\}.$$

The best values of α and $\phi\beta E$ for each series can be obtained by trial and error and are given in columns 13 and 14 of Table II.

Three typical series of points with the calculated curves fitting them are shown in Fig. 3.

With the exception of the two series of runs 1-7 and 8-14 the values of α are fairly consistent with one another. The former of the two discordant series requires α to be many times larger than is found in any subsequent series. The reason remains obscure. No single value of α will fit the series of runs 8-14, and since the other constants show a

similar unwonted variability, some unsuspected disturbing factor was presumably present, but to a lesser extent, here also. At the conclusion of the series, it was indeed observed that a thin white deposit, volatile when gently heated in vacuum, was present in the cell. This deposit was probably formaldehyde polymer.

To determine the temperature dependence of α and also to obtain more reliable values of this constant, it was decided to replace the reaction cell previously used by one with plane parallel ends and with inlet and outlet tubes placed in positions more likely to avoid "pockets" unaffected by the gas stream. The partial pressure of CH_2I_2 was also reduced to 0.67 mm. Hg (saturator temperature 15°) and the potassium chromate filter was used.

The energy of activation of α thus obtained is -1920 Cals. If, as is probable, the reaction between methylene and iodine requires no activation, the activation required for reaction with oxygen is $+1920$ Cals.

At 20° and 35° $e^{-\frac{1920}{RT}}$ equals 26.5 and 22.6 respectively, while the experimental values of α at these temperatures are 29.2 and 24.9. The close agreement shows that reactions (1) and (2) are kinetically almost identical. Too great reliance should not perhaps be placed on this energy of activation since, when the methylene iodide partial pressure was raised to 1.82 mm. and the filter removed, the value of α required at a reaction temperature of 35° was 25.7 which differs rather considerably from the previous value at this temperature of 24.9.

The greatly increased accuracy obtained with the second cell (runs 37-78) seems most easily explicable by the absence of the possibility of the existence of the "backwaters" which was favoured by the design of the first cell.

The remaining four constants can only be evaluated as the two ratios ;

$$k_4/k_5 \text{ and } k_6/k_7.$$

k_4/k_5 can be calculated from either of the relations

$$k_4/k_5 = \frac{2Y}{(C/L - 1)} \quad . \quad . \quad . \quad (9)$$

$$k_4/k_5 = \frac{\bar{X}Y}{\bar{X} - \bar{L}} \quad . \quad . \quad . \quad (10)$$

the bars denoting that the amounts of the substance formed or used up in unit time are to be used.

The two expressions give within the experimental error the same result, (9) being, however, the more accurate, especially where the amount of reaction is small as in runs 40-62. It is this value which is given in column 11 of Table II.

The quantum yield gives a further value of k_4/k_5 .

In the present work, the quantum yield was determined with so high an oxygen partial pressure that the expression for the iodine collected per hour can be safely simplified to $\phi\beta E$. The quantum yield with respect to iodine then becomes equal to

$$\beta = \frac{2Y + k_4/k_5}{Y + k_4/k_5}$$

whence

$$k_4/k_5 = \frac{Y(2 - \beta)}{\beta - 1} = 6.2 \times 10^{-4}.$$

From the results in column 11 of Table II. it can be seen that the same value of k_4/k_5 is not applicable throughout. There is, firstly, a very distinct difference between the values for the two cells, suggesting that the reactions are at least partly heterogeneous. This would explain the great variability of the ratio with the first cell, since the arrangement of its inlet and outlet tubes was not so favourable to a thorough sweeping out of the cell contents by the gas stream. The results obtained with the second cell are far more consistent but there is a definite tendency for the values of k_4/k_5 to be below the average at the lower pressures. This would be accounted for if a reaction between methylene peroxide and adsorbed methylene iodide occurred more readily than the heterogeneous transformation of methylene peroxide into formic acid. From the constancy of the ratio with total pressures between 8 and 20 mm. Hg. reactions 4 and 5 are presumably essentially homogeneous over this pressure range and reaction 4 is truly monomolecular. That the presence of foreign gases slightly accelerates the formation of formic acid is indicated by the considerably higher value of k_4/k_5 deduced from the quantum yield.

The average value of k_4/k_5 at 35° is a little below that at 20°. The difference is, however, not much larger than would be expected from the change in the collision number with temperature, and the excess may well be due to experimental error. If the practical absence of a temperature coefficient for this ratio is taken as meaning that neither reaction requires thermal activation, the minimum mean life of methylene peroxide with respect to its transformation into formic acid corresponding to a collision efficiency of unity for reaction 5 will be of the order of 5×10^{-7} seconds.

The evaluation of k_4/k_7 is most easily effected by means of the relation

$$k_4/k_7 = \frac{\bar{F}(2\bar{F} + \bar{C} - \bar{L})}{2_0V(\bar{C} - \bar{F} - \bar{L})}$$

where V_0 = the volume rate of flow through the reaction cell and \bar{C} , \bar{L} , and \bar{F} are respectively the gm. mols. of iodine, formic acid and formaldehyde collected in unit time. The values are given in Table II., column 12.

Apart from the absolute value (k_4/k_7 is about twenty times smaller than k_4/k_5) there is a surprising similarity between the two ratios. k_4/k_7 is also larger with the first cell than with the second and shows too the same tendency to be below its average value at the lower total pressures. The decomposition of ethylene peroxide is therefore also over most of the pressure range investigated a true homogeneous monomolecular reaction. Unfortunately no values of k_4/k_7 at high pressures could be obtained so that it is not possible to say whether the stability of this peroxide is also reduced by collision with other molecules as is apparently that of methylene peroxide. The decrease in the ratio at low pressures suggests that the surface of the cell favours reaction of the peroxide with formaldehyde rather than its decomposition.

Similar assumptions to those made with k_4/k_5 give ethylene peroxide a minimum mean life of the order of 10^{-6} seconds.

In order to obtain a value of k_4/k_5 from the quantum yield it was assumed that the efficiency of the primary process (I.) was unity. The quantum yield is not however very sensitive to changes in k_4/k_5 and if the efficiency were actually 0.88 instead of unity, k_4/k_5 as calculated from the quantum yield would be in agreement with the other values.

The reaction is now being investigated at higher pressures in order to settle this point.

Summary.

The products of the photo oxidation of methylene iodide have been studied and a mechanism accounting quantitatively for the products is proposed.

The intermediate formation of CH_2 , CH_2O , and $(\text{CH}_2\text{O})_2$ is assumed. The minimum value of the activation energy of the reaction of methylene with oxygen is 1920 Cals.

The peroxidic substances CH_2O , and $(\text{CH}_2\text{O})_2$ change over spontaneously into formic acid and formaldehyde respectively.

We wish to express our thanks to Imperial Chemical Industries, Limited, for grants to the laboratory with which the Spekker photometer and the diffusion pump were purchased.

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REVIEWS OF BOOKS.

Optical Basis of the Theory of Valency. By R. DE L. KRONIG. The Cambridge Series of Physical Chemistry. (Cambridge University Press, pp. i-x, 1-246. Price, 16s. net.)

Professor Kronig's book on *The Optical Basis of the Theory of Valency* deals with many topics which are already familiar to physical chemists, such as (i) the determination of intramolecular distances by X-ray analysis of vapours (Debye), or by the method of electron-diffraction (Mark and Wierl), (ii) the spectroscopic basis of the periodic classification, (iii) molecular spectra, including the isotope effect, and the determination of force constants and moments of inertia from the vibrational and rotational components of the spectrum, and finally (iv) the study of dissociation by spectroscopic methods, including the phenomenon of predissociation. This familiar material is, however, submitted to the chemist in an unusual form, since the author is himself a mathematical physicist. The chemical reader therefore finds himself subject to an unfamiliar discipline, and is given the opportunity of considering from a novel standpoint the foundations on which his science is built. It may be that the number of chemists who are qualified to benefit by this discipline is not large; but it is a real advantage that a book should be available, in which workers on the borderline between chemistry and physics may find the relevant material set out as clearly and accurately as in the present instance. It is also a solid advantage that the book is written in English, and is not so long as to impose an excessive burden on the reader. It can therefore be commended heartily to all chemists who would like to know what their science looks like in the eyes of a physicist, and also to physicists who wish to apply their own science to chemical problems.

T. M. L.

Metastrukturen der Materie. By PROFESSOR WOLFGANG OSTWALD. 16 pp. with 1 Figure; Dresden, 1935. Theodor Steinkopff. Price R.M. 0.80.

Those who have had the pleasure of listening to Professor Ostwald know well the dexterity with which he can produce an arresting phase in summarising what might be called the objectives of Colloid Science. In this monograph, an academic speech, we note the same breadth of philosophic treatment of the theme. It is with peculiar zest we remember that Professor Ostwald himself was one of those who in "those early days" defined colloids as the science of the Forgotten Dimension. This is not true now, the stone (or pyrogel) which the builders rejected is certainly now the headstone in the corner of our house. Colloids are now bristling with dimensions, and among organic substances they are the only ones which have the great advantage of presenting a real and tangible form and structure to the world.

The gaping void which existed between the terrestrial atoms and macro structures is now filled with colloids. It is interesting to speculate whether this seething abyss is the fons and origo of ourselves or represents nothing more than nature's garbage tin. Until recently it is true that the respectable organic chemist meeting a colloid would quietly pour it down the sink, but now the resins and plastics are saved and have to be synthesised and analysed. We as well as the resins and plastics are indebted to Professor Ostwald for this brave new world.

E. K. R.

Colloids in Agriculture. By C. E. MARSHALL, M.Sc., Ph.D. (London: Edward Arnold & Co. Pp. viii + 184. Price 5s. net.)

Dr. Marshall's knowledge and personal experience of colloids is a guarantee of the general soundness of this little book. It is planned in three sections. In the first an account is given in simple language of the main achievements of academic researches in the realm of colloids. The second part deals with colloids in the soil, and the third with colloids in plant and animal life. This way of arranging the subject matter has its drawbacks, the chief of which is that whereas a piece of academic research is described near the beginning of the book, it is not applied to anything connected with agriculture until near the end. In the intervening pages a host of other topics is discussed, and it needs considerable mental capacity to store up so many abstract ideas and then draw upon them one by one at a later stage. Some indeed are used so little that the student who is mainly interested in the agricultural side might justly feel that he had been persuaded to learn them under false pretences.

We cannot help feeling that the book would have been more readily assimilated by students of agriculture if it had been arranged in the reverse order, the colloidal behaviour exhibited by soil and the products of life being used to develop the fundamental notions the author wishes to instil. Such an approach would have produced a book corresponding better to the title.

The field covered is a wide one because agriculture is a many-sided occupation, and it is hardly to be expected that the book would be entirely free from errors. Two statements have caught our attention

which need correction. The first is that a plant which thrives in a hot, dry climate must lose very little water by evaporation from its leaves and must be able to take up water vapour from the air when the latter attains a greater humidity than usual; the second is that the isoelectric point of a protein is the point of minimum ionisation.

The author has a rather irritating way of discoursing on the views and feelings of "the physicist" and "the chemist." On page 45 we read, "But whereabouts in the solution shall we find these balancing ions? That is the question which tormented the physicists." It is difficult to see the purpose of such a remark.

R. KENWORTHY SCHOFIELD.

Outline Notes on Telephone Transmission Theory. By W. T. PALMER. Foreword by W. CRUIKSHANK. (London: Pitman (1936). Pp. 165. 22 cms. \times 14 cms. Price 4s. net.)

Both author and publisher have made great efforts in this book on telephone transmission theory to meet the demands of a large body of engineering students. The book largely derives from the author's lectures at the Northampton Polytechnic Institute and the clarity of the printing and the writing, together with the blank pages for notes indicate that the average student's requirements have been very carefully considered. The book is divided into seventeen sections, and it is impossible in a short review to indicate the nature of the contents of all of these. The first two sections of the book are concerned with the building up of the necessary mathematical knowledge and the classical theory of electric wave propagation. The mathematical section should be taken rather as a revision course than a development from first principles, and Mr. Palmer gives adequate references to other more comprehensive works. Other important parts of the book deal with D.C. transmission, wave distortion in cables, artificial lines, transmission efficiency of telephone circuits, electrical wave filters, telephone repeaters, and unloaded ocean telegraph cables. The book closes with a good index and the sectional references to individual works should be valuable. Important derivations in the text are heavily underlined and one gets the impression, however unjust, that the student is being told perhaps just enough as is considered good for him without adequate regard for the great historical development of this subject; Heaviside gets one mention—in the foreword—and Kelvin receives a similar treatment in the text. This might be good enough for engineers but physicists will have a few words to say about it. The book is well printed on good paper. In turning over the pages it would be a good deal easier to see what was being discussed if the page legends corresponded to the section titles; instead of this we are treated to a repetition of the book-title.

J. T. R.

Thermionic Emission. By T. J. JONES. London: Methuen's Monographs on Physical Subjects (1936). Pp. viii + 108. 17 \times 11 cms. Price 3s. net.

Students and others anxious to obtain a readable survey on the subject of thermionic emission may find in this little work the kind of thing they require. The disadvantages of compression are most obvious when a more

comprehensive up-to-date work is already in existence. Jones's book is divided into six chapters; these include a theoretical survey, a discussion on experimental technique and others on atomic film emitters, oxide coated cathodes and the thermal emission of positive ions. The book would have been improved by a more critical attitude towards the many researches that are discussed. Mr. Jones's choice of phrase is sometimes a little unusual; surely "oxygenated tungsten" would be better than "oxidised tungsten" where monatomic films are concerned. The bibliography is extensive for a work of this scope.

J. T. R.

Molekulspektren und ihre Anwendung auf chemische Probleme II.

Text. By H. SPONER. (Berlin: Julius Springer. 1935. Pp. xii and 506. Price 36.0 RM. (Paper covers), 37.8 RM. (Bound).

This, the latest addition to the *Struktur und Eigenschaften der Materie* Series, is an exceptionally interesting volume, largely for the reason that it contains a great deal of information rarely found between the same two covers. Perhaps the basic characteristic of the Natural Philosophy of the past decade has been the ruthlessness with which pre-existing boundaries between physics and chemistry have been forcibly shifted, and in some instances obliterated. Thus, it is to be expected that a considerable amount of space would be needed to define the *status quo ante*, and this occurs in the first four chapters, which deal with the older quantum theory, quantum mechanics, molecular spectra and the use of band-spectra in the determination of the usual physical and chemical magnitudes. Some of the treatment, though very clear, suffers a trifle from over-compression, which is noticeable in the sections dealing with entropy and the chemical constant. Actually this is bound up with the formalism of the gulf which separates geometrical concepts (like the shapes of molecules) from pure thermodynamics, with their independence of mechanism.

The remaining chapters contain material of more direct concern to the physical chemist. An excellent survey of the spectroscopic criteria for atom-molecules, ion-molecules and polarisation-molecules will be found under the general heading of types of binding. The author then discusses the various theories in detail, following this up with chapters on molecular collisions, and some further applications of spectroscopy to chemical problems. The book concludes with a number of comprehensive tables, which together with the data contained in Part I. (see these *Transactions* 1935, 31, 1374), form a valuable work of reference. The writer is to be congratulated upon the freshness with which he develops his theme. There are references in plenty, but the text is not written round them; they appear at the right moment as apt illustrations, and never as pegs upon which to hang the usual comments.

The chemist of to-day tends to rely upon almost any method which gives him direct information about the molecule as such: spectroscopy (combined with magnetic analysis) is probably the most powerful, and Professor Sponer has shown clearly the great strides which have been taken in recent years.

F. I. G. R.

Principles and Applications of Electrochemistry. Vol. II. Applications.

By W. A. KOEHLER. John Wiley & Sons, Inc., New York; Chapman & Hall, Ltd., London. 1935. Pp. xiv + 545. Price 25s.

The long awaited second volume of *Principles and Applications of Electrochemistry*, the first part of which is already in its third edition (*Trans. Faraday Soc.*, 1936, **32**, 522), has now appeared under the authorship of Professor W. A. Koehler, instead of Colin G. Fink, whose multifarious activities have prevented him from undertaking the work. There is little doubt, however, that the publishers have secured an adequate substitute, and the new volume gives a satisfactory survey of the many applications of electrochemistry. The scope of the book may best be judged from the titles of the chapters, which are as follows: Economics of Power Generation; Review of Theoretical Electrochemistry; Primary Cells; Secondary Cells; Electroplating; Electroplating Solutions; Electrorefining of Metals; Electrometallurgy—Aqueous Solutions; Electrometallurgy—Fused Electrolytes; Electrolysis of Alkali Halides; Electrolytic Oxidation and Reduction; Hydrogen and Oxygen; Corrosion; Electroanalysis; Electric Furnaces—General; Electric Furnaces in the Metallurgical Industries; Electric Furnaces in the Non-Metallurgical Industries; Electronics; Ozone; Fixation of Atmospheric Nitrogen; Separation by Electrical Means; and Miscellaneous Electrochemical Processes.

To cover such a vast amount of ground in the course of some 500 pages, many of which are largely occupied by figures, means, of course, that the treatment is often superficial, but there are frequent references to the literature where further information can be found. The author is indeed to be congratulated on the extent and variety of the information which he has succeeded in collecting and collating. The book is partly intended as a text-book for students, presumably technological, and partly as a reference work for those in industry: it should prove of great value to both types of readers if they wish to become acquainted with the scope of applied electrochemistry, without requiring great detail. The author sometimes forgets that this book is a companion to one devoted to the principles of electrochemistry, as is evident from the 43 pages of "Review of Theoretical Electrochemistry," but his object was, no doubt, to make the work self-contained and complete in itself. The production of the book is excellent, and the descriptive matter is illustrated with 244 diagrams and photographs: it is altogether a work to be commended.

S. G.

A RAPID MICRO-METHOD FOR THE DETERMINATION OF MELTING-POINT.

BY R. C. RAY AND V. DAYAL.

Received 27th January, 1936.

The determination of melting-points of substances which fuse at high temperatures, especially of inorganic salts, is a tedious operation. The present paper describes a simple and rapid method for determining the melting-points of minute quantities of solid substances. McDavid¹ measured the ignition temperatures of gaseous mixtures by means of an electrically heated spiral of platinum wire, the temperature of which was obtained by passing a known current, which was determined with an ammeter. It appears, however, that the method has not received the wider application which it deserves. McDavid's method has been adapted to the measurement of melting-points. Preliminary experiments seem to show that the method would also be applicable to determinations of freezing-point—solubility of solids.

The apparatus required is quite simple, and is shown diagrammatically in Fig. 1. A small piece of platinum wire is bent so as to form a point W.

The two ends of the wire are sealed to short pieces of glass tubing and electrically connected by means of mercury to the battery B, through two sliding resistances, R and R_1 , the milliammeter A and the switch key K. A minute quantity of the finely-powdered solid, the melting-point of which has to be determined, is spread in as thin a layer as possible upon the mica platform P which can be raised or lowered as necessary. The platinum point W is made to touch a tiny particle of the solid whose fusion is observed through the telescope T. The platinum point is heated by the current from a storage

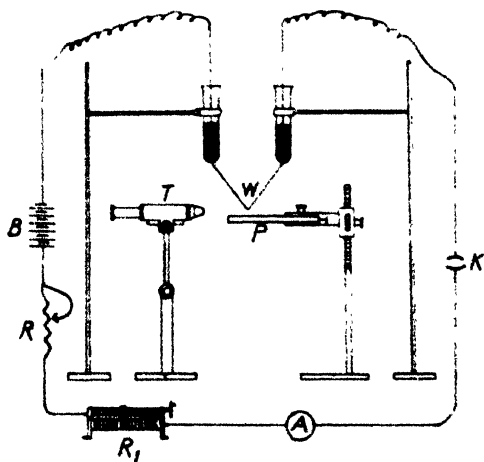


FIG. 1.

battery of 24 volts but of high capacity so as to obtain no fluctuation in the current during an experiment. The melting temperature is first roughly adjusted by the resistance R, the final adjustment being made by the finer sliding resistance R_1 . The current necessary to raise the platinum point to the temperature of fusion is measured by the milliammeter. In the preliminary experiments a platinum spiral was used and the powdered

¹ *J. Chem. Soc.*, 1917, 111, 1003.

substance was dusted on the spiral, but it was found that at the melting-point the molten substance spread, causing a short circuit.

The results obtained with 10 inorganic salts, which had been carefully purified by recrystallisation, are given in the following Table :—

Substance. . .	CdCl ₂ .	KIO ₃ .	CdBr ₂ .	KI.	KBr.	KCl.	NaCl.	Na ₂ CO ₃ .	SrCl ₂ .	K ₂ CO ₃ .
Current in amps. .	2.147	2.150	2.164	2.330	2.416	2.474	2.519	2.587	2.608	2.647
Melting-point C. (observed)	558°	560°	569°	680°	737°	776°	806°	851°	865°	891°
Melting-point C. (International Critical Tables)	568°	56(0°)	583°	773°(?)	7(30°)	×	804°	851°	873°	891°

A large number of determinations of the melting-point of each substance was made, and the values recorded above represent the mean of these results. The greatest difference obtained in the value of the current to attain the melting-point of any one substance was never more than 0.005 amps., which corresponds to a temperature difference of 3 to 4 degrees, and therefore $\pm 4^\circ$ may be regarded as the experimental error. The melting-point recorded in the International Critical Tables, Vol. I, 1926,

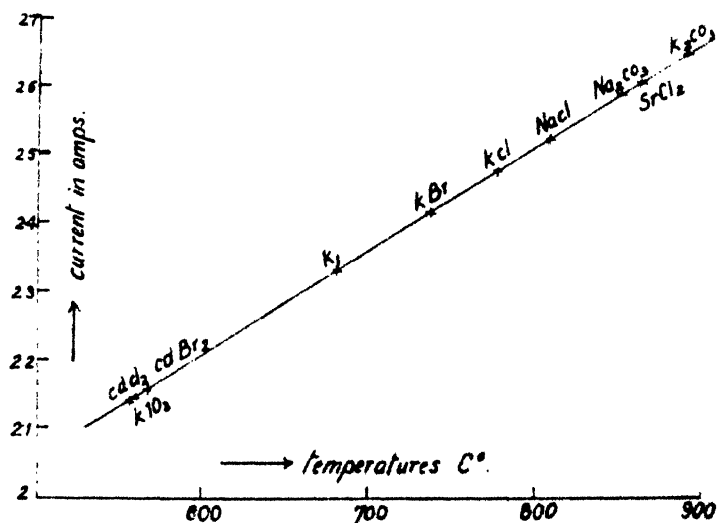


FIG. 2.

is also included for comparison. It should be pointed out in this connection, that there exists a considerable amount of discrepancy regarding melting-points of inorganic compounds; different melting-points have been obtained for the same substance by different investigators. Several workers, for example, have found 680° as the melting-point of potassium iodide, while the Critical Tables give the value 773°, which is certainly not the correct temperature.

The heating currents are plotted against the melting temperatures in Fig. 2. In obtaining the graph, the melting-points of three substances, which had been especially purified and whose melting-points had been previously determined by other methods, were taken as standards, and

temperatures corresponding to the observed heating currents gave the melting-points of other substances. It will be noticed that the relationship between the heating current and the melting-points is a straight line, and for it the equation $C = M \times 0.0015 + 1.310$, where C is the heating current and M is the melting temperature, holds, so that when the apparatus is once set up, the melting-point of any substance may be readily obtained by simply measuring the current passing through the platinum point when the substance just begins to melt. The great advantage of the method is that only a minute quantity of the substance is required for the determination of the melting-point.

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THE DISSOCIATION CONSTANT OF HYDROCHLORIC ACID.

By ROBERT A. ROBINSON.

Received 30th December, 1935.

One of the most important arguments in favour of the complete dissociation of strong electrolytes is to be found in the extremely small partial vapour pressures of the hydrogen halides in moderately dilute aqueous solution. Wynne-Jones¹ has utilised this small vapour pressure to calculate the dissociation constant of hydrochloric acid by assuming that Raoult's law gives the mole fraction of undissociated hydrochloric acid as the ratio p/p_0 , where p is the partial vapour pressure in aqueous solution and p_0 the vapour pressure of pure hydrogen chloride at the same temperature. Hence Wynne-Jones concluded that the dissociation constant of hydrochloric acid at 0° is 2.5×10^7 . As this acid is so often quoted as an example of complete dissociation, it is worth while utilising the vapour pressure data at other concentrations and temperatures, for the argument will be more convincing if it can be shown that the "dissociation constant," calculated in this way, is constant over a range of concentration and varies in the expected manner with temperature.

I have used the partial vapour pressure data at 0°, 10°, 20°, 25°, 30°, 40° and 50°, recorded in the International Critical Tables,² over the concentration range 0.56-15.4 *M*-HCl as well as the vapour pressure of pure hydrogen chloride at these temperatures.³ In addition the data of Dunn and Ridcal⁴ at 25° have been used to obtain points at low concentrations. From these the mol. fraction of undissociated hydrochloric acid was calculated and thence the dissociation constant from the equation:

$$K = \frac{a_H a_{Cl}}{[HCl]},$$

[HCl] being the mol. fraction of the undissociated component and a_H and a_{Cl} being calculated from the activity coefficient data of Randall and Young.⁵ Two assumptions are made: (1) that the activity coeffi-

¹ *J. Chem. Soc.*, 1930, 1064.

² *I.C.T.*, III., p. 301.

³ *Ibid.*, p. 228.

⁴ *J. Chem. Soc.*, 1924, 125, 676.

⁵ *J. Amer. Chem. Soc.*, 1928, 50, 989.

cient of the undissociated acid is unity, (2) that the activity coefficients of the dissociated parts do not vary with temperature. Both these errors will diminish with increasing dilution, but whereas the former is not likely to be affected appreciably by temperature, the second error may even change its sign with a temperature increase. Fig. 1 shows the results of these calculations.

From this figure it is evident that the effect of the two errors mentioned above are at a minimum at 20°, 25° and 30° and extrapolation gives a probable value for K at these temperatures. The fact that at 0° and

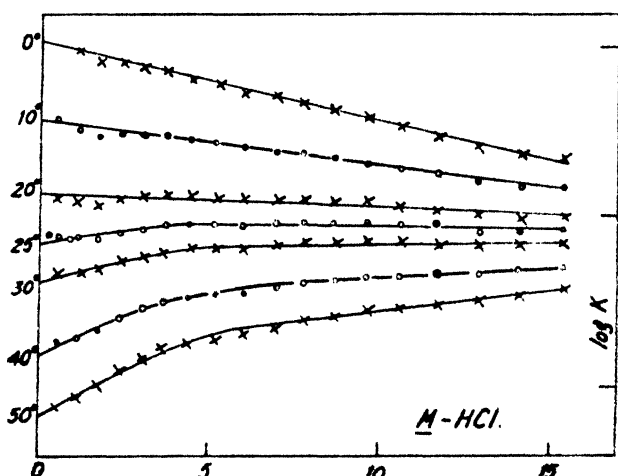


FIG. 1.—Variation of the dissociation constant of hydrochloric acid with concentration and temperature.

10° K decreases with increasing acid concentration whereas the converse is true at 40° and 50° is probably due to the changing value of the ionic activity coefficients. In view of the experimental difficulties involved in determining partial vapour pressures at low concentrations the 'constancy' of K is all that

can be expected. The following values are obtained by extrapolation for the dissociation constant, the concentrations being measured in the more usual units of gram mols. per 1000 g. of water.

° C.	0	10	20	25	30	40	50
$K \times 10^{-4}$	20	6.8	2.4	1.3	0.72	0.28	0.12

If $\log K$ is plotted against $\frac{1}{T}$ the points lie on a straight line whose slope gives the thermal changes associated with the complete process of dissociation as 17,900 cal. As K diminishes with a rise in temperature, i.e., temperature favours the formation of the undissociated molecule, this amount of heat must be evolved in the process of dissociation. It is to be anticipated that the dissociation would be highly exothermic in view of the extent to which the reaction proceeds.

Summary.

The calculation of the dissociation constant of hydrochloric acid from partial vapour pressure data has been extended to a wider range of concentration and temperature. The thermal changes associated with the complete process of dissociation of hydrochloric acid are found to be 17,900 cal. (evolved).

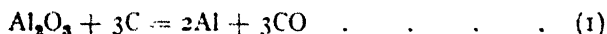
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A STUDY OF THE CRYOLITE-ALUMINA CELL WITH PARTICULAR REFERENCE TO DECOMPOSITION VOLTAGE.

BY J. W. CUTHBERTSON, M.Sc.,* AND J. WADDINGTON, M.Sc.

Received 10th December, 1935.

The earliest research on the theory of the electrolytic process for the extraction of aluminium from alumina-cryolite baths appears to have been undertaken by F. Haber¹ and his collaborators who, working on the laboratory scale, endeavoured to show that the electrolysis obeyed Faraday's laws. Their efforts were unsuccessful, failure probably being attributable to the formation of metal fog. Furthermore, the effects of secondary electrode reactions and mixing of the primary products by convection currents, factors which are relatively far more important in small-scale experiments than in industrial cells, were not fully appreciated. By weighing the anode before and after an experiment, F. Haber and R. Geipert² found that a little more than 0.66 grm. of electrode material was consumed in the production of 1 grm. of aluminium, and as this agrees with the equation:



concluded that this reaction correctly expressed the cell decomposition. For a long time the view was held that economy in anode consumption was thus definitely limited.

In 1916 G. H. Bailey³ suggested that the above reaction did not truly represent the electrolysis, for in the first instance the gases evolved from the cell normally contain a large proportion of carbon dioxide, and secondly, the weight of carbon actually consumed in the process is insufficient to account for the formation of carbon monoxide alone. The following year, R. Seligman⁴ published analyses of anode gases from an experimental furnace. In one case the carbon dioxide content was 45.6 per cent. and carbon monoxide 43.6 per cent. Raising the operating temperature by 110° C. decreased the quantity of carbon dioxide in the gases and increased both the carbon monoxide content and anode consumption. J. D. Edwards, F. C. Frary and Z. Jeffries⁵ suggested that an even higher carbon dioxide figure applied to the working of industrial cells. They put the limits at 50-90 per cent. Seligman's original view was that oxygen was primarily formed, according to the equation:



and that "whether oxygen, carbon dioxide or carbon monoxide resulted was dependent upon such factors as temperature, current density, physical properties of the carbon anode, rapidity with which the gases

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¹ *Z. Elektrochem.*, 1902, 8, 607.

² *Ibid.*, 1902, 8, 26.

³ *J. Inst. Met.*, 1916, 15, 303.

⁴ *Ibid.*, 1917, 17, 141.

⁵ *Aluminium Industry*, 1930, 1, 311.

were removed from contact with the anode and similar factors." Bailey, on the other hand, believed that carbon dioxide was first formed, thus:



for under favourable conditions the proportion of this gas present may be very large, in spite of the fact that at the temperature of the cell the equilibrium:



is well over towards the right-hand side.

Later work on the cell decomposition voltage has shown that the carbon exerts a depolarising effect, reducing the voltage required for decomposition. The formation of oxides of carbon is an inherent characteristic of the electrolysis, and hence it is probable that the true conditions are represented by a combination of reactions (2) and (3) with the latter predominating under normal conditions.

The decomposition voltage may be determined experimentally but the practical difficulties involved are considerable, and consequently several investigators have attempted to calculate its value from thermodynamical data. J. W. Richards,⁶ in 1903, calculated 2.3 v. as the decomposition voltage for an unattackable anode. This result, taken in conjunction with his figure of 0.6 v. for the depolarisation arising from the use of a carbon anode, agrees almost perfectly with his experimental findings. G. Gin,⁷ using Le Blanc's commutator method, obtained a value of 2.3 v., whilst J. W. Langley⁸ working along very similar lines, observed the much lower figure of 1.2 v. at 1010° C. P. P. Fedotieff and W. Iljinsky,⁹ in a general account of the electrometallurgy of aluminium based upon an exhaustive investigation of the process, have attempted to explain these discrepancies. Although they were unable to obtain characteristic curves for the voltage-current relationship, they noticed that electrolysis started well below 2.0 v. and claimed to have observed the formation of particles of aluminium, accompanied by gas evolution at the anode, at 1.2-1.3 v. They concluded that the metal so liberated reacted with the carbon to form aluminium carbide, and hence permanent metal separation would not occur until the voltage was increased considerably, the actual figure given being 2.2 v. In support of this view, it may be said that the voltage corresponding to the energy of formation of the carbide has been calculated by Berthelot to be 0.9, so that if aluminium is permanently liberated at 2.2 v. the carbide should form at a potential of 1.3 v. Fedotieff and Iljinsky, however, state that the metallic particles first set free react with the carbon with almost explosive violence, and in view of more recent work, it would appear highly probable that this phenomenon is due at least in part, not to the formation of aluminium carbide, but to simple oxidation of the metal. Consequently, *permanent* metal separation may begin at as low a voltage as 1.2.

In 1927 P. Drossbach¹⁰ gave 2.565 v. for the decomposition voltage of a cell having inert anodes but later, for a saturated solution of alumina in cryolite at 927° C., recorded the lower value of 2.16 v.¹¹ Comparatively recently A. B. Newman and G. G. Brown,¹² in America, have

⁶ *Electrochemical Industry*, 1903, 1, 158.

⁷ *Ber. Internat. Kongress f. angewandte Chem.*, IV., 502 (see also ⁹).

⁸ *Trans. Electrochem. Soc.*, 1902, 2, 256.

⁹ *Z. anorg. Chem.*, 1913, 80, 113.

¹¹ *Ibid.*, 1930, 36, 179.

¹⁰ *Z. Elektrochem.*, 1927, 33, 114.

¹² *Ind. Eng. Chem.*, 1930, 22, 995.

calculated values of 2.04 v. and 2.06 v. for saturated and half-saturated solutions respectively, the temperature in each case being 950° C. These authors have also computed the depolarisation arising from oxidation of carbon anodes and state that the decomposition voltage may thereby be reduced to 0.947 v.

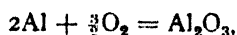
The decomposition voltage E at any given temperature may be calculated from the formula :

$$E = \frac{\Delta F}{nf} = \frac{\Delta F}{138,444} \text{ volts} \quad (1)$$

where ΔF is the free energy of formation of alumina from aluminium and gaseous oxygen at that temperature. For any given temperature T ,

$$\Delta F = \Delta H - T\Delta S$$

where ΔH is the heat of the reaction :



and ΔS is the change in entropy. At constant pressure the change in free energy with temperature is :

$$\Delta F_T = \Delta F_{298} - \int_{298}^T \Delta S dT.$$

The last term is conveniently evaluated by graphical integration of the entropy-temperature curve derived from existing data, and hence ΔF_T can be found and E for any temperature calculated from equation (1). The heat of combustion of aluminium has been determined with renewed care by A. Meichsner and W. A. Roth,¹³ who obtained the value of $393,300 \pm 400$ cal. at 20° C. and constant pressure. They attribute their former low result, used by Drossbach, and also by Newman and Brown in their calculations, to exothermic reactions resulting from ignition in clay boats. Taking the above value of ΔH , for a saturated solution of alumina in cryolite, the theoretical decomposition voltage at the normal working temperature of 960° C. becomes 2.16 v. For any other alumina concentration C_1 the decomposition voltage will be :

$$E_1 = E + \frac{RT}{nf} \ln \frac{C}{C_1}$$

where E is the calculated voltage for a solution of concentration C . Within limits, the effect of a reduction in concentration is not very pronounced. Thus,

$$\begin{aligned} E_1 &= E + 0.012 \text{ for a half saturated solution} \\ &= E + 0.024 \text{ for a quarter saturated solution.} \end{aligned}$$

From data given by Eastman,¹⁴ the depolarisation by graphite has been calculated. Assuming a temperature of 950° C., the figures found are :

$$\begin{aligned} E &= 0.99 \text{ volt. } (\text{C} + \text{O}_2 \longrightarrow \text{CO}_2) \\ E &= 1.10 \text{ volt. } (\text{C} + \text{O} \longrightarrow \text{CO}). \end{aligned}$$

The depolarisation should therefore lie somewhere between these limits. Taking Edwards, Frary and Jeffries' estimation of the composition of furnace gases found in works practice, i.e. 50-90 per cent. CO_2 , it would appear as though 1.0 volt would be a reasonably accurate figure to adopt.

¹³ *Z. Elektrochem.*, 1934, 40, 19.

¹⁴ *U.S. Bur. Mines Inf. Circ.*, 6125, 1929 (see also ¹²).

Investigation of the conductivity of the molten cryolite bath is beset with even greater practical difficulties than is the determination of the decomposition voltage, consequently it is not surprising that the amount of work published on the subject is small. The accuracy attainable with ordinary a.c. bridge methods depends largely on the absolute value of the resistance to be measured, and is of a relatively low order when the total cell resistance, that is, the resistance of cell plus liquid, is low. It is desirable, therefore, that the value of the total resistance should not be less than approximately 10 ohms, and hence the container should preferably be of some non-conducting material. Unfortunately, the extremely corrosive nature of molten cryolite introduces a complication and most, if not all, of the feebly conducting refractories available for the container are rapidly attacked.

K. Arndt and W. Kalass,¹⁵ using a platinum crucible and central disc electrode, determined the specific resistance of cryolite at 1000° C., obtaining a value of 0.448 ohms per cm.³ As alumina was added to the melt, the conductivity fell almost linearly and, by extrapolation, became zero at 100 per cent. alumina. Also the equivalent conductivities of cryolite and sodium fluoride were found to be approximately equal, and hence it was concluded that the alumina acted as solvent and the cryolite as ionised solute, the conductivity being attributed to the rapidly migrating sodium ion, the anion AlF_6''' being assumed to move slowly. In these experiments, the resistance of the cell was only of the order of 0.3 ohm and, therefore, the accuracy of the results is open to question, particularly as the authors themselves admit some difficulty in balancing the bridge. Furthermore, the possibility of alumina additions leading to the formation of aluminate incrustations on the walls of the crucible or central electrode must not be overlooked, and as the resistance of the cell would thereby be increased, this factor might have a profound effect on the observed increase in specific resistance referred to above.

In the case of the decomposition voltage, the inherent difficulties associated with its determination are no doubt largely responsible for the discrepancies between the results of different investigators. The same probably applies to conductivity measurements. The present work was undertaken mainly to obtain further information on these two important factors. The greater portion of the work is devoted to the determinations of the decomposition voltage of cryolite and cryolite-alumina mixtures, but a few experiments on the conductivity of molten cryolite have also been completed.

Determination of the Decomposition Voltage.

The industrial type of aluminium cell, in which the bath is maintained in a molten state by the Joule effect of the current traversing it, is unsuitable for research purposes. Compared with large units the heat losses from small cells are relatively very much greater, therefore to prevent the bath from freezing the current must be increased. This leads to excessively high anode and cathode current densities and the final conditions may be totally different from those under which the technical process is operated. Furthermore, temperature control of small baths with internal electric heating is difficult, and the temperature is not uniform throughout the melt. All of these disadvantages may be overcome by applying external heat to maintain the bath temperature, and as the electrolysing current is then independent of the heating, the former may be varied at will.

¹⁵ *Z. Elektrochem.*, 1924, 30, 12.

In the present work the electrolysis was carried out in a carbon crucible heated in an electric furnace having a resistor element of nichrome tape wound on a 4-in. diameter sillimanite tube, a refractory which resists fairly well attack by the vapours evolved from the melt. For the majority of the experiments a graphite crucible was employed, but as amorphous carbon is used in industrial cells, crucibles of this material were also tried out. On the whole, the graphite and amorphous carbon containers gave substantially the same experimental results, but the latter absorb the greater amount of electrolyte, have the higher specific resistance, and disintegrate more rapidly than graphite crucibles.

For the manufacture of the pots, 3-in. diameter graphite rod was machined to the form shown in Fig. 1, the cavity being made slightly conical to facilitate removal of the solidified melt. Nichrome tape, freed from oxide, inserted into holes bored in the crucible walls and plugged firmly with carbon rods, served to make a sound electrical connection. A third hole was also provided to house the thermocouple sheath. Undue volatilisation of the charge was prevented by a lid of baked alundum cement, through the hole in which the central electrode was inserted. During melting this electrode was withdrawn and the aperture in the lid closed by a smaller alundum disc, thus effectively sealing the crucible and reducing the losses to a minimum.

The simplest and most direct method of determining the decomposition voltage is from current-voltage curves. By using the crucible as one electrode in conjunction with a small point electrode which may be either the anode or the cathode, it is possible to obtain the discharge potentials of the respective anions and cations.

For the construction of the central electrode, details of which are given

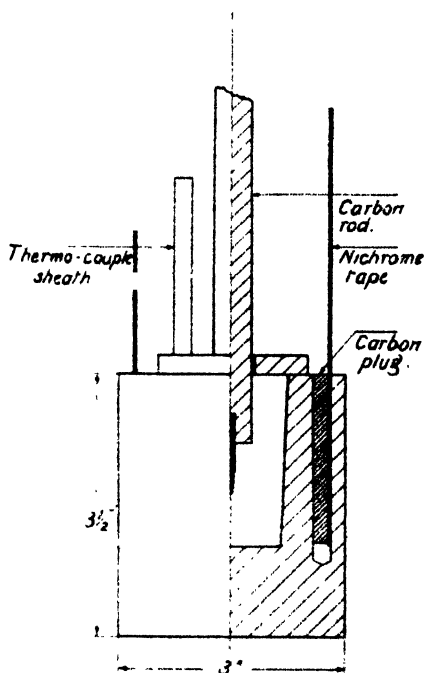


FIG. 1.

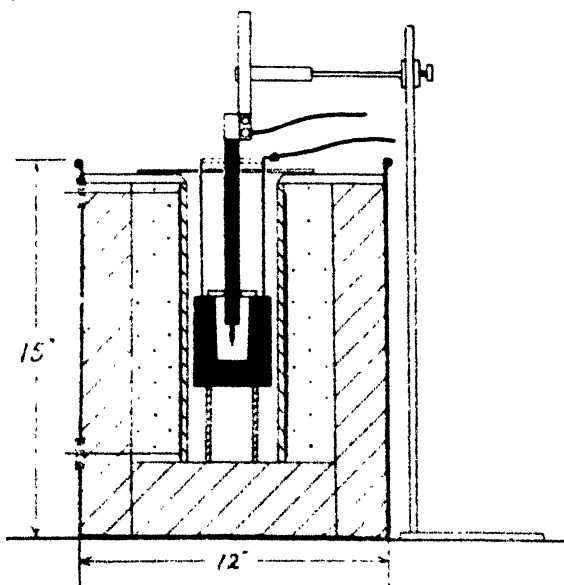


FIG. 2.

in Figs. 1 and 2, a short length of $\frac{1}{8}$ -in. diameter graphite rod was forced tightly into a hole bored axially in a larger carbon rod, the protruding end being ground to a blunt point. The ratio of the areas of the two electrodes actually in contact with the melt was 20:1. Protection of the large central rod was afforded by the application of two or three coats of a paint made from powdered carborundum and a 25 per cent. solution of sodium silicate, a mixture which is very effective in preventing undue oxidation.

The crucible was supported inside the furnace on a short length of silica tube but separated therefrom by sheet mica, thus ensuring, so far as possible, electrical insulation from the furnace winding.

A diagram of the circuit used for the current-voltage determinations is reproduced in Fig. 3. Current for electrolysis was drawn from a 10-volt accumulator service, the necessary variation in voltage being provided by the potential divider R_2 and series resistance R_1 . Switch S_1 is for the purpose of reversing the polarity of the cell, and by means of S_1 connection may be made between the cell and either the current source or the Wheatstone bridge on the left. The instruments A and V_1 indicate the current

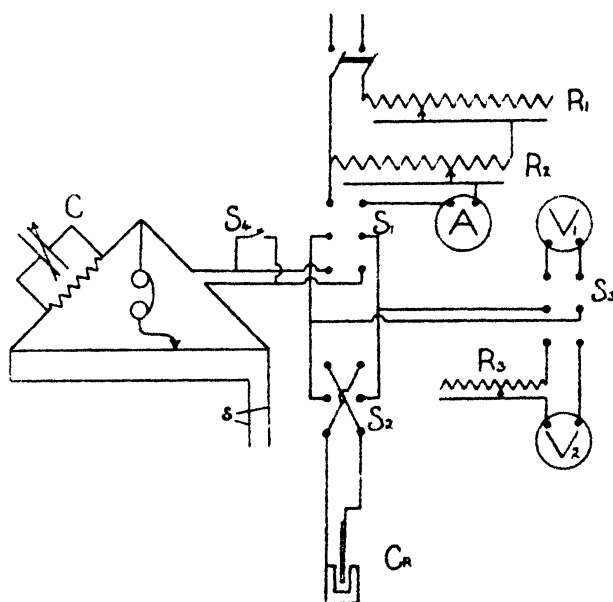


FIG. 3.

and voltage respectively. The voltmeter V_2 , of greater sensitivity than V_1 , may be introduced as required by the switch S_2 , its range depending on the adjustment of the variable resistance R_3 .

To obtain a true value for the voltage expended in decomposition, the voltage drop in the leads, electrodes and electrolyte itself must be known. The a.c. resistance of the cell circuit was determined by means of the Wheatstone bridge in conjunction with alternat-

ing current supplied from a separate valve oscillator. Since the resistance to be measured was only of the order of half an ohm the resistance of the bridge circuit should also be low and any small capacities must be balanced out. A standard 1 ohm resistance shunted by a variable condenser C was used in the second arm of the bridge.

The valve oscillator circuit is reproduced in Fig. 4. The rotary switch S is connected to tappings on the anode coil. As its contact revolves two distinct notes of different frequency are repeated at regular intervals in the 'phones, and it then becomes a relatively simple matter to balance the bridge, no additional amplifier being required.

In conducting an experiment, sufficient cryolite or cryolite-alumina mixture in the form of powder is put into the crucible, which is then covered with the lid, and the whole placed in the furnace previously heated to about 1000°C . When molten the charge is stirred and, as soon as the temperature becomes steady at the value decided upon, the resistance is measured. The next procedure is the determination of the current-

voltage curve which is completed step by step, the voltage being adjusted each time by manipulation of R_1 and R_2 . Readings of current and e.m.f. are taken as soon as a steady state is reached. Except when the voltmeter V_1 is in use, V_1 may conveniently be left permanently connected across the cell circuit and, if after recording, the circuit is broken by means of S_1 , the cell back e.m.f. will be given directly by this instrument. It should be emphasised that, although V_1 is of lesser sensitivity than V_2 , its internal resistance is sufficiently high to ensure the effect on the deflections of A being immeasurably small.

If the back e.m.f. does not die away quickly enough, the cell is short-circuited by closing the switch S_4 . When the applied voltage is low, this is usually unnecessary, but beyond a certain value some considerable time elapses before the back e.m.f. entirely disappears.

The length of time occupied in taking a large number of readings gives ample opportunity for the resistance and composition of the electrolyte to alter, and accordingly a limited number of accurate readings is preferable to more numerous hurried observations. On the completion of a series of readings the resistance of the circuit was always re-checked, and if there was evidence of any appreciable change the results of the experiment were discarded.

If the small central electrode is made the anode the resistance after electrolysis can only be restored to the original value, and the bridge satisfactorily balanced, by passing a current through

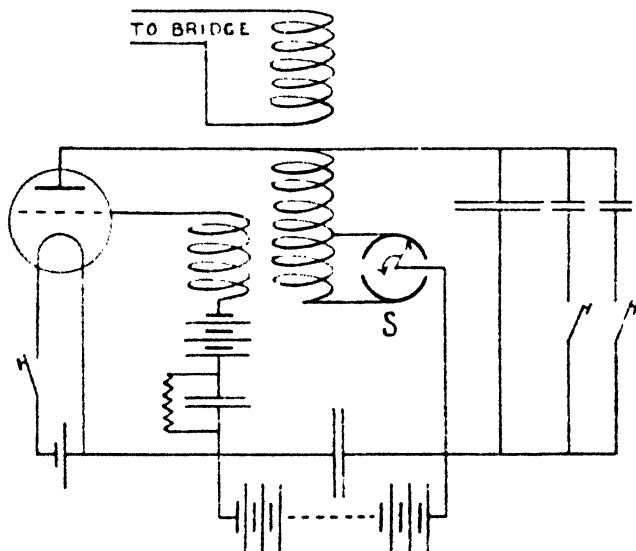


FIG. 4.

the cell in the reverse direction for a short time. Unless this is done, an approximate balance only can be obtained, corresponding to a cell resistance very much above that initially recorded.

When the applied potential difference exceeds some 2 v., on switching off the current the back e.m.f. falls rapidly to about 1 v., remaining stationary just below this value before finally dropping quickly to zero. The instrument V_1 was installed specifically to investigate this phenomenon, and enabled the rate of fall of back e.m.f., after applying a certain fixed voltage for perhaps 20 seconds, to be followed closely. Curves obtained in this manner (see Fig. 10) show a definite peak, the magnitude and position of which depend upon the bath temperature and composition. This, however, only applies to those cases in which the small electrode is the cathode. If made the anode the back e.m.f. dies away almost instantaneously.

Determination of the Conductivity of Molten Cryolite.

Attempts to measure the conductivity along the lines developed by Arndt and Kalass, but substituting a graphite container for their platinum

crucible, met with little success, the results varying greatly from one experiment to another. Failure is attributed to two causes: firstly, to the unsatisfactory nature of graphite for cell construction owing chiefly to its high specific conductivity, and secondly, to the shape or design of the container which, in crucible form, is fundamentally wrong. According to Kohlrausch, when using measuring current of audio-frequency, accurate results free from polarisation errors are only obtainable if the area of each electrode is greater than $10/R \text{ cm.}^2$ where R is the resistance of the electrolyte in ohms. In the case of the Arndt and Kalass cell the flux resistance was about 0.1 ohm , so that for accurate work the electrode area should exceed 100 cm.^2 Expressed in a different form, their cell will only furnish correct results when the resistivity of the charge is greater than $25 \text{ ohms per cm.}^3$

To check the findings of these investigators a different type of cell was

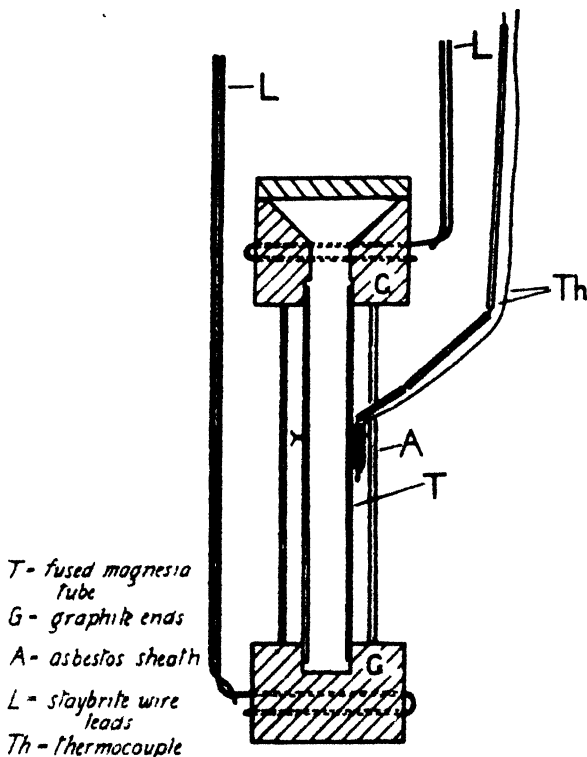


FIG. 5.

decided upon, the chief aim being to increase the overall resistance of the flux. A tubular container with end electrodes was finally constructed, a design which fulfils this requirement and also allows for the evaluation of contact resistance and potential effects by simply varying the length of the tube. Where the cell serves as one pole and a small central electrode constitutes the other, much of the resistance is concentrated around the latter, and hence a contact resistance in this locality would profoundly affect the issue.

As previously hinted, it is an extremely difficult matter to find a suitable material for the

conductivity cell. Most substances, if not rapidly attacked, are so porous as to allow the liquid charge to percolate through, a difficulty which is intensified in the tubular form of cell owing to the increase in the hydrostatic pressure of the charge. Of the materials examined, *vis.*, carbon, fused magnesia, and powdered carborundum sintered at 2000°C. , both with and without admixture of kaolin, magnesia gave the best results. Carbon has a low resistance, and furthermore is liable to attack by both oxygen and fluorine and whilst the latter may be negligible during the period of time occupied over a determination, loss of weight through oxidation, and resulting increase in the total resistance of the container itself is unavoidable in an open furnace. Sintered silicon carbide withstands chemical attack quite well, but is very porous, and efforts to reduce the porosity by mixing the powder with 10 per cent. of kaolin in the hope

that heat would fuse the aluminium silicate causing it to block the pores proved unsuccessful, the clay apparently interfering with the sintering process.

A number of experiments was carried out with so-called fused magnesia tubes. Even this material is porous, and also tends to dissolve slowly in the melt. The porosity may be reduced by an initial soaking in a hot saturated solution of magnesium nitrate followed by ignition at a high temperature. Sintered corundum (Al_2O_3) linings for electrolytic cells have been used by P. Drossbach,¹⁸ but the mechanical properties of this material are poor, and although not rapidly dissolved by cryolite already containing alumina, its contaminating effect on the pure flux renders it less suitable than magnesia for conductivity cells.

The construction of the cell is clearly outlined in Fig. 5, which is self-explanatory. The complete cell, which may be some 5 or 6 in. in length, is conveniently heated in the furnace previously illustrated (Fig. 2). When the required temperature is reached, the cell is filled with molten cryolite and resistance and temperature measurements taken. The cell is then withdrawn, emptied and returned to the furnace for determination of the resistance of cell plus connecting leads. A final measurement of the total resistance when the cell is filled with molten copper-aluminium alloy allows the resistance of the leads to be determined. The cell constant may be calculated fairly accurately from the linear dimensions. The area of cross-section is best determined by weighing the tube, of which the length is known, both before and after filling with mercury.

The figures recorded below will serve as a typical example of the application of this cell to conductivity measurement:—

Length of tube	= 10.29 cm.
Area of cross-section	= 0.774 cm. ²
Cell constant	= 0.0752
Temperature	= 1020° C.
Resistance of cell + leads - cryolite (R_1)	= 4.9 ohms.
Resistance of cell + leads (R_2)	= 185.5 ohms.
Resistance of cell + leads + metal (R_3)	= 0.219 ohm.
(When filled with highly conducting metal the re-resistance of the cell plus charge will be so low that it is legitimate to neglect it. Hence R_3 becomes the resistance of the leads.)	
Resistance of cell ($R_2 - R_3$)	= 185.28 ohms.
Resistance of cell + cryolite ($R_1 - R_3$)	= 4.68 ohms.
Resistance of cryolite $\left(\frac{1}{\frac{1}{(R_1 - R_3)} - \frac{1}{(R_2 - R_3)}} \right)$	= 4.80 ohms.
Specific resistance of cryolite at 1020° C.	= 4.8 × 0.0752.
	= 0.361 ohm per cm. ³

Discussion of Results.

Two typical current-voltage curves selected from a series obtained with a small cathode are reproduced in Fig. 6. In every case investigated the curve showed a number of distinct breaks, ultimately becoming parallel to the line representing resistance, that is, to R , R in the figure. The actual values corresponding to the various discontinuities in the particular cases here represented are given in Table I., where E is the observed e.m.f. and E_s is the true or corrected value, derived from the equation:

$$E_s = E - IR,$$

I being the electrolysing current and R the resistance as measured by the bridge.

¹⁸ *Z. Elektrochem.*, 1934, 40, 605.

TABLE I.—POSITION OF BREAKS IN CURRENT-VOLTAGE CURVES. TEMPERATURE 1025° C.

Cryolite.			Cryolite + 16 per cent. Alumina.		
E , Volts.	I , Amps.	E_b , Volts.	E , Volts.	I , Amps.	E_b , Volts.
0.99	0.11	0.93	0.56	0.03	0.54
1.90	0.60	1.55	1.12	0.23	1.01
2.25	0.99	1.68	1.78	0.74	1.41
			2.38	1.80	1.48
$E_d = 1.70$ volts.			$E_d = 1.51$ volts.		

Taking firstly the results for fused cryolite at 1025° C., three breaks are discernable, dividing the curve into four sections, the positions of the first and last breaks especially showing extremely close agreement in the case of all the curves for this and also for other charges. The first branch of the curve is almost horizontal, and what little current passes is probably due to continuous depolarisation—the applied voltage is below the deposition voltage of the cation, hence there is no deposition and no back e.m.f. Only a limited current can flow in this way, for if the current

density is increased the voltage at the electrode rises above the deposition value of the cation which consequently is deposited. When this occurs, more current flows, increasing in value proportionately to the potential difference in excess of the deposition voltage, and the second stage of the curve is entered upon. During this period, the current falls gradually soon after switching on, and continuous electrolysis is, therefore, impossible. The results plotted in the curves were all taken immediately after the commencement of electrolysis, a precaution which, if conditions are liable to change with time, is

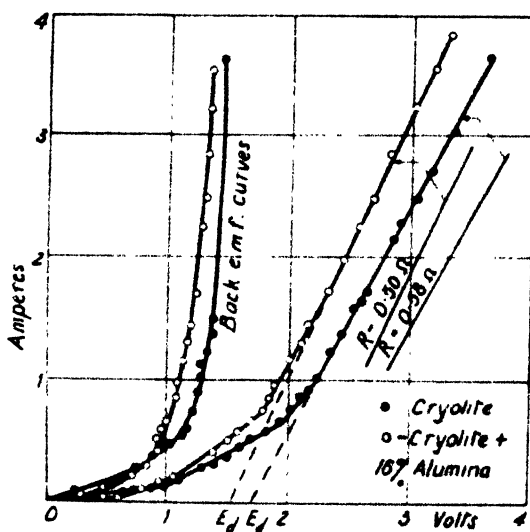


FIG. 6.—Current-voltage curves obtained with a small cathode. Temp. 1025° C.

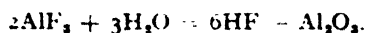
clearly essential. The second break, which would appear to indicate the presence of two cations in molten cryolite, is succeeded by the third and fourth stages in which the current becomes much steadier and the back e.m.f. falls slowly. The last branch of the curve is approximately parallel to the line representing resistance, indicating that the full conductivity of the melt has been developed, both cations and anions taking part in current conductivity. The value found by producing this part of the curve backwards to cut the voltage co-ordinate at E_d is the total decomposition voltage of fused cryolite at 1025° C., and should theoretically be equal to the corrected voltage corresponding to the last break in the curve.

The authors made several abortive efforts to compound a synthetic cryolite having properties similar to those of the natural product. It was anticipated that investigation of the behaviour of the synthetic material would shed light on the mechanism of electrolysis previously studied, but the experiments proved to be disappointing. Sodium and aluminium fluorides were mixed in the proportions demanded by the composition of cryolite ($3\text{NaF} \cdot \text{AlF}_3$), and after melting in the crucible, a current-voltage curve was taken in the usual manner. In every case the curves for the synthetic and the natural materials differed, and in particular it was observed that, in the former case the voltage corresponding to the peak in the back e.m.f. curve was markedly reduced. On concluding an experiment the melt was analysed, the average results being given in Table II.

TABLE II. ANALYSIS OF CRYOLITE.

	Fluorine.	Sodium.	Aluminium.
Synthetic	46.0 per cent.	33.0 per cent.	13.5 per cent.
Natural	54.28 ..	32.84 ..	12.81 ..

In the first case the missing 7.5 per cent. is probably due to oxygen (not estimated), present in combination with a part of the aluminium forming alumina. Fedotieff and Iljinsky⁹ have found that aluminium fluoride readily absorbs water which, owing to hydrolysis, cannot be removed by heating in air, thus :



As it is apparently very difficult to obtain the fluoride absolutely free from water, there will always be the danger of heat converting the synthetic mixture into a dilute solution of alumina in the double fluoride, which probably accounts for the observed discrepancies between the current-voltage curves of the two materials.

Turning now to cryolite-alumina melts, attention was concentrated on a mixture containing 16 per cent. of alumina, which, although somewhat richer than is employed industrially, has a relatively low melting-point and therefore allows increased latitude for exploration. The composition is approxi-

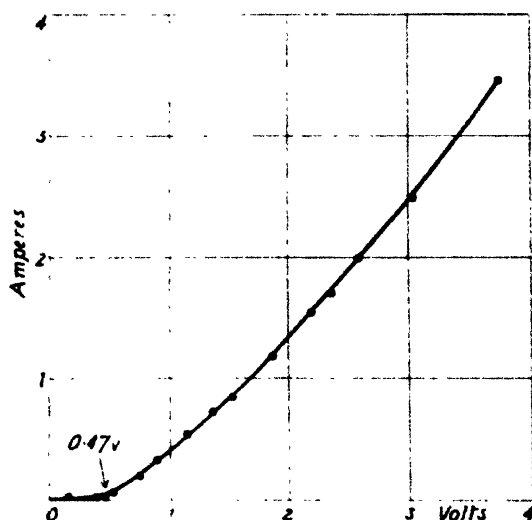


FIG. 7.—Current-voltage curve of a 16% alumina-cryolite melt obtained with a small anode. Temp. 1025° C.

mately that of the cryolite-alumina eutectic. The cathode current-voltage curve for this mixture differs from that for cryolite, there being evidence of a greater number of discontinuities of which the first occurs at a lower value than the corresponding break in the cryolite curve. Excluding the

first and last breaks, the position of the other discontinuities in the curves of all cryolite-alumina mixtures examined, up to 24 per cent. alumina content, was not so definite as in the case of curves obtained from pure cryolite melts.

The anodic curve for the 16 per cent. alumina melt is reproduced in Fig. 7, and the effect of temperature on the relative positions of the discontinuities in both the cathodic and anodic curves is illustrated by Fig. 8.

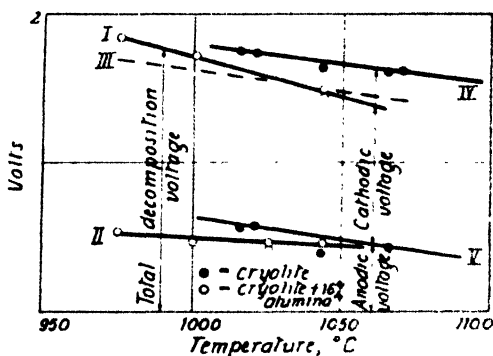


FIG. 8.—Effect of temperature on decomposition voltage of cryolite and cryolite-alumina melts.

of increase in alumina content on the cathodic and anodic voltages. From 8 per cent. alumina upwards there is only a slight increase in total decomposition voltage, as would be anticipated from theoretical considerations. The anodic voltages were determined from the position of the break in curves obtained with a small anode.

The back e.m.f. after electrolysis becomes approximately constant at 1.3-1.4 v. in the case of cryolite, and at 1.2-1.3 v. when the melt contains 16 per cent. of alumina. Back e.m.f. curves are included in Fig. 6, but more interesting results can be obtained by plotting the inverse rate of fall of e.m.f. against cell voltage, as shown in Fig. 10. In general form these curves resemble that which would be obtained from a secondary cell undergoing discharge through a fixed resistance, the peak voltage corresponding to the free energy of the reaction taking place. Although the quantity of electricity passed through the cell during electrolysis may be the same in every case, the magnitude of the peak is found to vary considerably with the composition of the charge.

The fact that no corresponding peak is found in the anodic curves seems to indicate that the form of these curves is associated with the accumulation of some product at the cathode, either sodium or aluminium. As the authors are unable to find evidence of a peak in the cathodic curve of sodium fluoride, the phenomenon must be attributed to the presence of aluminium. The diminution in the size of the peak resulting from addition

The temperature coefficient of the experimentally determined decomposition voltage, *i.e.*, the slope of the curve I. in the figure, is apparently greater than that found for cryolite, curve IV. It is quite possible, however, that the high results for the lower temperatures are attributable to incomplete solution of the alumina, and it is suggested that the dotted line, curve III., may more accurately represent the true state of affairs.

Fig. 9 shows the effect

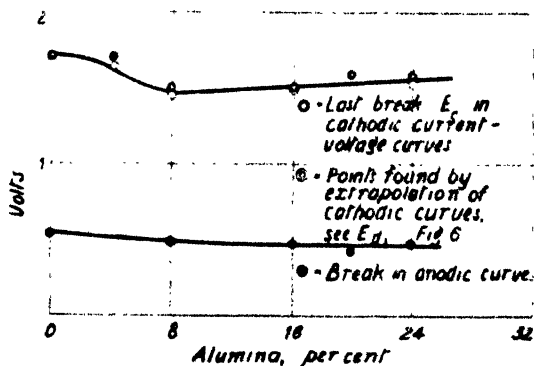


FIG. 9.—Change in decomposition voltage of a cryolite-alumina melt with increasing alumina content. Temp. 1025° C.

of alumina is not easily explained. In a manner at present not fully understood, alumina apparently tends to suppress the reversion of the cathodic product to the ionic state. Many back e.m.f. curves were plotted for melts of increasing alumina content, and the magnitude of the peak was found to reach a minimum value when the bath contained between 8 per cent. and 12 per cent. of alumina. Further alumina additions, up to 24 per cent., have no effect on peak dimensions, but there is a slight progressive lowering of the e.m.f. at which the peak occurs. It is significant that the ratio of alumina to cryolite in the melt giving the minimum arrest in the back e.m.f. curve agrees fairly closely with the composition of charge corresponding to the minimum in the decomposition voltage-alumina content curve, Fig. 9.

It was not originally the authors' intention to investigate in detail the behaviour of salt baths having unattackable anodes, but in view of a paper on depolarisation in the electrolysis of alumina, published by M. de K. Thompson and R. G. Seyl¹⁷ since the completion of the experimental part of this work, further tests were undertaken. The graphite anode previously used was replaced by a stout platinum wire welded to a staybrite rod, the

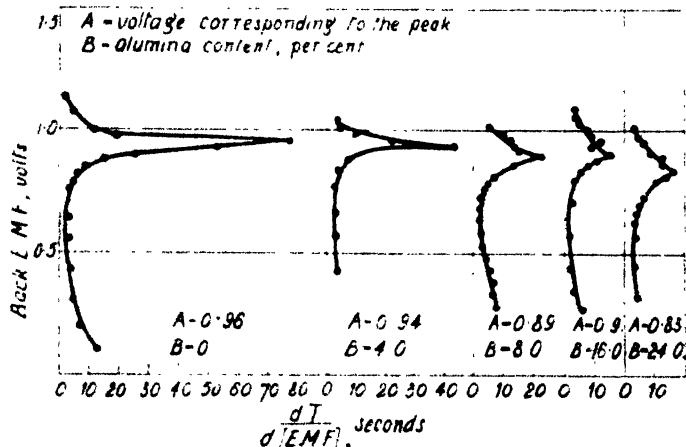


FIG. 10.—Effect of increase in alumina content on rate of fall of back e.m.f. after electrolysis.

remainder of the equipment being unchanged. Current-voltage curves for both cryolite and cryolite-alumina melts at 1025° C. were taken in the usual manner. Table III. gives the results derived from these curves, together with the average of those previously obtained with graphite anodes.

In the last case, the anodic depolarisation is 0.7 volt, which is somewhat lower than Thompson and Seyl's figure, viz., 0.87 volt, and still less than their calculated value of 1.15 volts—facts which support the conclusion that the depolarisation does not readily attain its full value, but varies probably with the condition of reactivity of the carbon. The figures for the decomposition voltage with carbon anodes are in reasonable agreement with the results published by Edwards, Frary and Jeffries representing works practice.

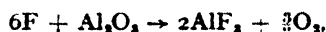
It is interesting to note that the electrolysis of fused cryolite with a platinum anode leads to very rapid destruction of the latter, whereas a similar anode immersed in a 16 per cent. alumina-cryolite melt for an hour, passing a current of 3 amps., was visually quite unaffected. In the former case the attack is undoubtedly due to fluorine liberated on the discharge of

¹⁷ *Trans. Electrochem. Soc.*, 1933, 64, 321.

TABLE III.—COMPARISON OF ELECTROLYSIS WITH PLATINUM AND GRAPHITE ANODES.

Electrolyte (Temp. 1025° C.).	Cathodic Voltage.	Graphite Anode.		Platinum Anode.		Anodic Depolar- isation.
		Anodic Voltage.	Decomp. Voltage.	Anodic Voltage.	Decomp. Voltage.	
Saturated cryolite- alumina solution (calculated).	—	—	1·12 (approx.)	—	2·12	1·0
Cryolite.	1·13	0·57	1·70	1·10	2·23	0·53
Cryolite-alumina (16 per cent.)	1·05	0·45	1·50	1·15	2·20	0·7

a fluorine-bearing anion, probably AlF_6''' . Addition of alumina apparently diverts fluorine attack from the anode material to itself, thus :



with regeneration of the aluminium fluoride.

The results of the experiments on the conductivity of molten cryolite are recorded in Table IV. The average value of all the determinations is 0·361 ohm per cm.³ Taking the results for a temperature of 1025° C., the average becomes 0·352 ohm per cm.³ These figures are distinctly lower than those of Arndt and Kalass,¹⁶ whose average result for the same material at 1020° C. is 0·435 ohm per cm.³ As previously indicated, the discrepancy is probably attributable to polarisation, particularly in view of the statements of these investigators regarding the difficulties experienced in balancing the electrical circuit.

TABLE IV.—SPECIFIC RESISTANCE OF FUSED CRYOLITE.

		Temperature °C.	Specific Resistance, ohm per cm. ³
Tube No. 1.	First experiment.	1025	0·321
	Second "	1025	0·351
	Third "	1030	0·352
Tube No. 2.	First "	1025	0·379
	Second "	1020	0·361
	Third "	1025	0·356
Tube No. 3.	First "	1020	0·412
	Second "	1025	0·354

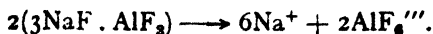
Conclusions.

The isolation of aluminium in the electrolytic cell can only be explained by postulating that either (a) the alumina is ionised in solution, probably giving rise to the ions Al^{+++} and AlO_3''' , and is primarily decomposed by the current, or (b) the cryolite is ionised, the alumina being unionised or ionised to a slight extent only. Numerous investigators have advanced evidence in favour of both theories, but in recent years the second has gained ground.

As alumina is added to cryolite, the conductivity of the melt falls. On the other hand, the conductivity is proportional to the sodium

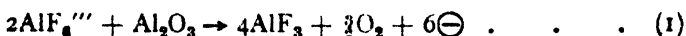
fluoride content of the bath. It is difficult to believe, therefore, that the first theory can represent the true facts. The authors are inclined towards the view that the cryolite is the ionised solute carrying the current, an assumption in close accordance with the experimental observations.

The cryolite is probably completely ionised, thus :



There are other possibilities, however, and although the evidence cannot be regarded as conclusive without further confirmation, there is some indication from the current-voltage curves of the existence of two cations in molten cryolite.

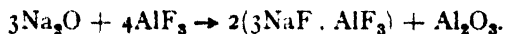
On adding alumina to the bath, the oxide is decomposed at both electrodes. Considering firstly the anodic process, the chief reaction is :



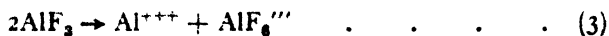
the final product at the anode being oxygen or, in the presence of a carbon anode, a mixture of oxides of carbon. At the cathode we have :



Interaction of the secondary products of equations (1) and (2) regenerates the cryolite, thus :



Alternatively, the dissociation of the cryolite may give rise to the cation Al^{+++} , thus :



the sodium fluoride taking no active part in the electrolysis, a highly improbable suggestion. Apart from other considerations, the separation of sodium at the cathode during the operation of the technical process under certain conditions is by no means a rare occurrence.

Compared with the other ions in the melt, the sodium ion is relatively fast-moving, and tends to accumulate at the cathode where it is either discharged, the metallic sodium decomposing the alumina as in equation (2), or alternatively, there may be an exchange of charge between the sodium and aluminium ions, the latter proceeding from the slightly ionised alumina. Whichever view is adopted, the result is the same—the alumina plays the rôle of both anodic and cathodic depolariser, supplying aluminium at the cathode and regenerating aluminium fluoride at the anode.

Summary.

(1) The decomposition voltages of cryolite and of a 16 per cent. alumina-cryolite mixture, electrolysed with platinum anodes at 1025° C., are 2.23 and 2.20 volts respectively.

(2) The same melts, electrolysed with graphite anodes at 1025° C., are decomposed at 1.7 and 1.5 volts respectively.

(3) The depolarisation never attains the theoretical maximum value, but varies probably with the state of reactivity of the anode material.

(4) The decomposition voltage of cryolite falls approximately linearly with increasing temperature.

(5) At 1025° C. the decomposition voltage-alumina content curve falls to a minimum at about 8 per cent. alumina. From 8.24 per cent. alumina there is a slight progressive increase in decomposition voltage.

(6) The conductivity of molten cryolite at 1025° C. is 0.352 ohm per cm.³

(7) In the aluminium cell the current is carried by the ionised cryolite. The alumina is either unionised or ionised to a slight extent only.

The authors are indebted to Mr. G. B. Brook, F.I.C., of the British Aluminium Co. Ltd., whose help and advice have greatly facilitated the progress of this work.

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THE BINDING OF GLACIAL PHOSPHORIC ACID BY THE PROTEINS OF WHEAT FLOUR.*

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The property of coagulating water soluble proteins has long been used to distinguish glacial phosphoric acid from the other phosphoric and simple mineral acids. It was pointed out by one of us in an earlier paper¹ that, after adding an excess of this acid to a protein, an aliquot can readily be separated for back titration in order to determine the acid taken up by the protein. As it seemed possible that a determination of the acid binding capacity of the proteins in wheat flour might prove of practical utility, a number of measurements of this kind have been made.

Glacial Phosphoric Acid.

The glacial phosphoric acid was procured from time to time in 100 gm. bottles of sticks or lumps. The solutions used (except where stated otherwise) were made by dissolving crushed fragments of the acid in cold distilled water at the rate of about 8 gm. per litre. The results of titrations of a freshly prepared solution with NaOH and $\text{Ca}(\text{OH})_2$ in which the change in p_H was followed with the aid of a glass electrode, is shown in Fig. 1. It is generally agreed that glacial phosphoric acid solutions contain not only monometaphosphoric acid— HPO_3 —but also polymers of general formula $(\text{HPO}_3)_n$. Thus, although there is only one titratable hydron to each phosphorus atom, a whole series of dissociation constants determine the form of the titration curve. These, however, fall into two main groups. A certain proportion of the hydrions having a relatively strong dissociation can be titrated with NaOH, using an indicator turning at about p_H 4.5, whereas an indicator turning above p_H 9 is needed to determine all the titratable hydrions. These end-points were first obtained by Sabatier,² who also observed that the titre to the second end-point increases with time, owing to hydrolysis, while the titre to the first remains unchanged. With solutions containing only 8 gm. per litre, the change in one hour at room temperature is, however, barely detectable.

* This paper embodies with other matter the substance of a thesis by L. W. Samuel, approved for the degree of Ph.D. in the University of London.

† Hackett Research Student of the University of Western Australia.

¹ R. K. Schofield, *Trans. Faraday Soc.*, 1935, **31**, 390.

² P. Sabatier, *Compt. Rend.*, 1888, **106**, 63; 1889, **108**, 738 and 804.

A titration curve for a freshly prepared solution of each batch of acid was obtained on first opening the bottle, using a quinhydrone electrode and NaOH (the glass electrode only becoming available towards the end of the investigation). These were all of the same general form as the upper curve in Fig. 1 (except that, owing to the limitations of quinhydrone, they could not be traced above p_H 8), but were not identical in shape, as may be exemplified in the fact that the ratio of the titre to p_H 4.5 to that at p_H 8.0 varied from 0.61 to 0.70 for six bottles of stick acid, and was 0.56 for a bottle of lump acid. This variation is not surprising, as the proportions in which the constituent acids are present must depend on the exact conditions of preparation which are difficult to reproduce exactly.

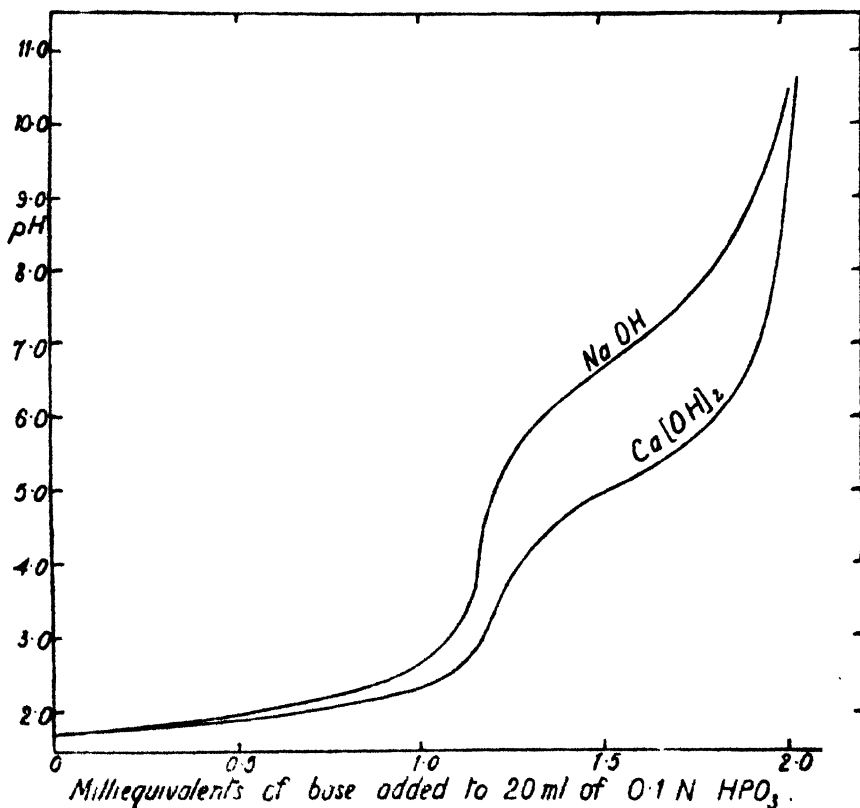


FIG. 1.

Measurement of Acid Uptake.

The determination of acid uptake by back titration has special advantages when applied to a material such as wheat flour, which contains both soluble and insoluble buffering material. For, provided the p_H of the end-point of the back titration is the same as that of the material before it was mixed with the acid, the uptake measured is that of the precipitate only. From this it will be seen that neither end-point obtained with NaOH is suitable for wheat flour which is usually at about p_H 6 in its natural state. With $Ca(OH)_2$ the second end-point is reached a little above p_H 8 and can be obtained as low as p_H 6 by adding calcium chloride. In practice a satisfactory end-point can be obtained simply with $Ca(OH)_2$ (nearly saturated—about $N/22$) using thymol blue. This is because flour extracts have only a small buffering between p_H 6 and 8.*

* This statement only applies strictly to high-grade flours.

In this way it was ascertained that interaction between the acid and the proteins in wheat flour is very rapid. 100 gm. of flour was added to 500 c.c. of acid, and the bottle containing the mixture was kept for some weeks and shaken occasionally. At suitable time intervals small amounts were removed and centrifuged, and 10 c.c. of the clear liquid was titrated with $\text{Ca}(\text{OH})_2$ to thymol blue. Nitrogen was determined on each occasion on a further 20 c.c. Immediately after the first mixture had been made up, a second 100 gm. of flour was added to a further 500 c.c. of acid, and the mixture was shaken intermittently for 10 minutes. About 400 c.c. was then separated by centrifuging, bottled, and stored beside the first mixture. 10 c.c. samples of this liquid were withdrawn at intervals and titrated. 500 c.c. of the original acid was also kept and similarly titrated. It will be seen from Table I. that although all three titres increased with

TABLE I.

Time.	Titre of Acid in Contact with Flour.	Titre of Acid Separated after 10 mins. Contact.	Titre of Acid Alone.	Nitrogen in Acid in Contact with Flour. (mg. per 1 gm. flour).
15 mins.	19.70	19.70	23.35	0.62
30 mins.	19.70	19.70	23.35	0.62
1 hour .	19.70	19.70	23.40	0.62
2 hours .	19.75	19.75	23.45	0.61
4 hours .	19.80	19.80	23.60	0.62
7 hours .	19.85	19.85	23.75	0.62
24 hours .	20.20	20.20	24.30	0.72
3 days .	21.20	21.10	26.03	0.84
7 days .	22.75	22.55	29.00	1.16
14 days .	27.8	22.0	32.23	6.72
30 days .	40.0	32.9	38.68	14.37

time, owing to the hydrolysis of the metaphosphoric acid, there is for many hours no difference between the acid remaining in contact with the flour and that separated from it after 10 minutes' contact. This is most simply explained by supposing that the reaction was complete in 10 minutes, and that the acid bound by the flour protein undergoes practically no hydrolysis. It would be a very singular coincidence if, for many hours, slow hydrolysis of the bound acid exactly counteracted an increase in the amount bound. When a difference at length appears, an increase has occurred in the amount of nitrogen not precipitated which would itself affect the titre.

On the basis of this experiment, 10 minutes was adopted as the time of contact in measurements on a series of flours. In each case, 8 gm. of flour was shaken with 40 ml. of glacial phosphoric acid solution, centrifuged and filtered. 10 ml. of the filtrate was titrated with $\text{Ca}(\text{OH})_2$ to thymol blue, as was also 10 ml. of the original acid. The uptake per 100 gm. of flour was calculated by multiplying the difference between the two titres by one hundred times the normality of the $\text{Ca}(\text{OH})_2$ (determined on each lot) and divided by 2 (the grams of flour corresponding to the 10 ml. titrated).

The Uptake of Potassium Chloride, Hydrochloric Acid, Trichloroacetic Acid Compared with that of Glacial Phosphoric Acid—Water Binding.

This simple method of computation was only adopted after some preliminary experimentation. The first test was made by shaking up some flour with 0.1 N potassium chloride in order to discover whether the solution is concentrated through the "binding" of some water by the flour or diluted by a release of some of its air-dry moisture. A dilution was found,

but it was greater than could be accounted for by a release of all the air-dry moisture. The effect was even more pronounced with *N/20* solution. Thus some potassium chloride was taken up by the flour, and the experiment failed to give the information sought.

Some tests were then made by shaking up wheat starch with several acids at a series of concentrations. Of the whole flour, about 85 per cent. is starch which may, therefore, largely control the binding or release of water. Hydrochloric acid was found to be taken up in amounts which increased rapidly with increase in acid concentration above 0.1*N*, but which approached a steady low value at lower concentrations. The limiting low value (of the order of 0.01 milliequivalents per gram of starch) presumably reveals a small capacity to combine with hydrions. The increase in uptake at higher concentrations, like the uptake of potassium chloride, must be ascribed to loose binding of the chloride ions. Similar large uptakes of hydrochloric acid by proteins from strong solutions have been reported by Jordan Lloyd and Mays,² Atkin and Douglas,⁴ Hoffmann and Gortner,⁵ and others. An essentially similar behaviour was found with trichloroacetic acid. We have pointed out⁶ that this acid, being an effective protein precipitant even at 0.1*N*, and at the same time a simple monobasic acid, may prove useful in determining the hydrion binding power of pure proteins.⁶ Its uptake by starch places difficulties in the way of its use with flour.

The behaviour of glacial phosphoric acid is different. While solutions containing less than about 8 gm./litre (0.1*N* to the second end-point) are diluted a little on shaking with wheat starch, the strength of more concentrated solutions is slightly increased. The results can be accounted for by supposing that, for concentrations of this order of magnitude one gram of starch combines with a small amount of acid (roughly 0.01 milliequivalents) which does not vary much with the acid concentration, and at the same time binds about 0.1 gm. of water in addition to its air-dry moisture. These two processes acting together leave a 0.1*N* solution practically unchanged in concentration.

The Capacity of Wheat Proteins to Bind Glacial Phosphoric Acid.

Thus it appears that provided the concentration of glacial phosphoric acid is about 0.1*N* (8 gm./litre), the starch added in the flour is without appreciable effect, and the change in the concentration is due to combination of acid with the proteins. If the flour proteins, when added to the acid, are not combined with either acid or base, the acid taken up will equal the acid binding capacity; otherwise a correction is necessary. The lowest p_H at which all anions could be washed out of flour was found by Loeb's⁷ ferrocyanide method to be close to p_H 6. The amount of acid or alkali needed to bring each flour to p_H 6 was therefore determined. It usually lay between +0.2 and -0.2 milliequivalents per 100 grams of flour, which is a very small fraction of the acid uptake which averaged about 8.

As the amount of protein present may be taken as substantially proportional to the nitrogen content, the acid binding capacity (the uptake corrected to p_H 6) is plotted in Fig. 2 against the nitrogen precipitated

² D. Jordan Lloyd and C. Mays, *Proc. Roy. Soc.*, 1922, 93B, 69.

⁴ W. R. Atkin and G. W. Douglas, *J. Inter. Soc. Leather Trades Chemists*, 1924, 8, 359.

⁵ W. A. Hoffman and R. A. Gortner, *Colloid Symp. Mon.*, 1925, 2, 209.

⁶ R. K. Schofield and L. W. Samuel, *Nature*, 1934, 134, 665.

⁷ A. D. Ritchie has drawn our attention to a physiological investigation in which he titrated trichloroacetic acid extracts of proteins (*J. Physiol.*, 1929, 68, 295). The purpose was not, however, to determine the acid binding power of the proteins.

¹ J. Loeb, *Proteins and the Theory of Colloidal Behaviour*, McGraw Hill & Co., 1922, p. 30.

from one gram (*i.e.* the total nitrogen in 1 gm. less the amount found in 5 ml. of the extract which varied from 1.2 to 3.5 per cent. of the total). While there is a general tendency for the acid binding capacity to be greater the greater the amount of protein present, the flours with high nitrogen content on the whole bound less acid per unit weight of protein. At the same time, the variation in the acid binding of flours with the same nitrogen content is far outside the errors of titration (equivalent to 0.1 milliequivalents per 100 grams of flour at most). It has long been recognised that while the nitrogen content is a general indication of certain properties of a flour, there is considerable variation between flours with the same protein content. It is suggestive that the flour with 1.9 per cent. of nitrogen and an acid uptake of only 6.65 milliequivalents per cent. had a decidedly smaller water absorption than would have been expected simply from its nitrogen content. It is hoped that when better methods are

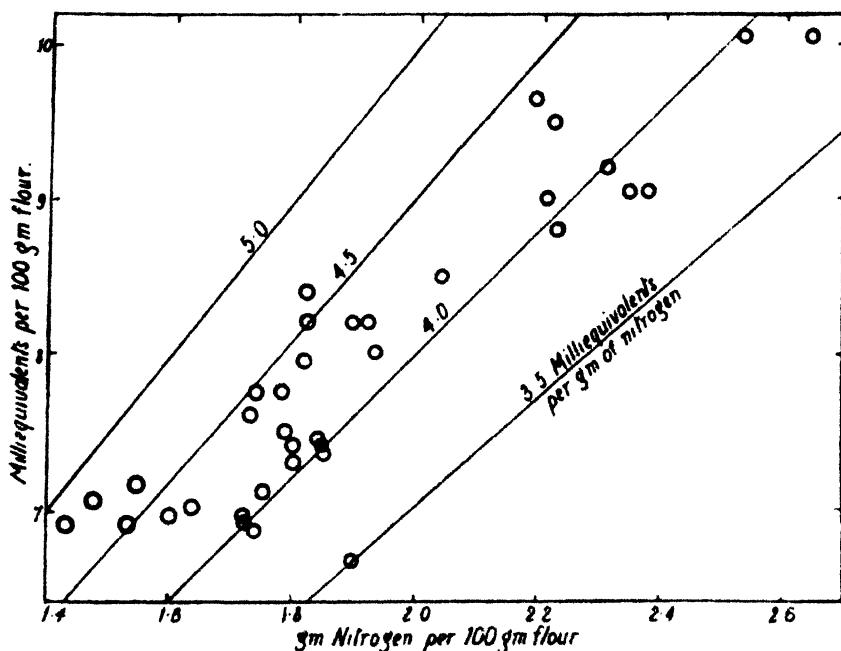


FIG. 2.

available for specifying quantitatively the physical properties of flour doughs such as those which, following the work of Schofield and Scott Blair^a are being worked out jointly in this laboratory, and in that of the Research Association of British Flour Millers, it will be possible to decide whether a determination of acid binding capacity is of technical value.

The Selective Action of Proteins on the Constituents of Glacial Phosphoric Acid.

In the meantime it appeared of interest to study more closely the interaction between glacial phosphoric acid and proteins. To this end, the water soluble constituents were removed from a flour by repeated washing, and the insoluble residue was shaken with 0.1*N* glacial phosphoric acid. In this case there is no restriction on the p_H to which the back titration should be taken. Titration curves were therefore obtained for the acid

^a R. K. Schofield and G. W. Scott Blair, *Proc. Roy. Soc.*, 1932, 138A, 707; 1933, 139, 557 and 141, 72.

before and after contact, with the aid of a quinhydrone electrode, using NaOH as alkali. A comparison of these two curves revealed differences, not only in the absolute magnitudes of the titres to the same p_H , but also showed that whereas for the original acid the titre to p_H 4.5 was 0.623 of the titre to p_H 8, the corresponding ratio after contact with washed flour was 0.601. The washed flour was very wet when added to the acid, but dilution from this cause would not have affected the *ratio* of the titres. It thus appeared that flour proteins do not bind the various (HPO_3) units in the proportion in which they exist in the original glacial phosphoric acid solution, but remove relatively more of those that buffer below p_H 4.5.

In a further study of this selective action, experiments were carried out with gluten (the total water insoluble wheat protein) and glutenin (the residue of gluten insoluble in 70 per cent. alcohol) which were both procured from commercial sources in a powdered air-dry condition. A sample of gliadin (the fraction of gluten soluble in 70 per cent. alcohol) was prepared from some of the gluten. For our immediate purpose it was sufficient, instead of tracing the whole curve electrometrically, to determine the titres to the two inflection points with the aid of indicators. The first inflection at p_H 4.5 is readily detected by bromo-cresol green. For the second inflection use was made of phenol-phthalein mixed with enough methyl red and bromo-thymol blue to give a neutral grey at p_H 9.5, the half-colour point. This is perhaps a little on the acid side of the actual inflection, but the curve is, nevertheless, steep enough at this p_H for a sensitivity to be obtained of one drop in a total titre of 20-25 c.c. Some typical results are shown in Table II. Before discussing the differences between the three

TABLE II.—ACID UPTAKE OF GLUTEN, GLUTENIN AND GLIADIN IN MILLI-EQUIVALENTS PER GRAM OF NITROGEN.

<i>Glacial phosphoric acid, 0.1N.</i>	<i>Gluten. Glutenin. Gliadin.</i>			
	0.588	0.521	0.598	
(1) Ratio of titres to p_H 4.5 and p_H 9.5 with NaOH of acid used.				
(2) Acid uptake from titre to p_H 4.5 with NaOH.	3.65	3.91	3.95	3.27
(3) Acid uptake from titre to p_H 9.5 with NaOH.	4.21	4.29	4.84	3.39
(4) Ratio of uptakes to p_H 4.5 and p_H 9.5.	0.87	0.91	0.82	0.97
(5) Acid uptake from titre to p_H 8.5 with $Ca(OH)_2$.	4.17	4.34	4.88	3.31
<i>Trichloroacetic acid, 0.05N.</i>				
(6) Acid uptake from titre to p_H 6.		3.2	3.4	—

materials, it is desired to draw attention to the discrepancies between the first two columns. These refer to the same material, but the measurements were made on different days with acid from different bottles. The difference between the two solutions of acid is exemplified in the figures of row (1). The discrepancies, particularly those in row (2), are greater than can be accounted for by titrational errors. Although the extreme values for eight lime titrations row (5), carried out at intervals over a period of several months—namely 4.17 and 4.34—only differ by 5 per cent., which is small in comparison with the variation in the uptake per gram of nitrogen shown by the flours of Fig. 2 (extreme values 3.52 and 4.82), it would probably be as well in future measurements with glacial phosphoric acid on flours to include a measurement on a stock gluten amongst those for each acid solution in order to relate more exactly measurements made with different solutions.

This source of error does not arise in comparing the two middle columns of the table, one for the gluten and the other for the glutenin, as the same

acid solution was used with both. It will be seen that the ratios given in row (4) are decidedly different both from each other and from the ratio in row (1). Now the figures in row (3) (or row (5) for they are substantially equivalent) give the *total* number of HPO_3 units taken up per gram of nitrogen. The figures in row (2) only give the number of those taken up which have a relatively strong hydrion dissociation. The ratio given in row (4) is therefore the proportion of the HPO_3 units taken up which have a strong dissociation, while the ratio in row (1) is the proportion in the original acid having strong dissociation. The conclusion derived from the experiment with the washed flour is thus confirmed, and in addition it becomes apparent the proteins differ in the degree of their selective action. The experiment recorded in the last column shows an extreme selectivity on the part of the gliadin which took up almost exclusively HPO_3 units having a strong dissociation.

It was argued in the paper already referred to,¹ that the precipitating action of glacial phosphoric acid indicates the presence of an anion which becomes firmly bound to basic nitrogen groups by some force over and above mere electrostatic attraction. Reasons were given for thinking that not all HPO_3 units would be capable of this firm binding and, further, that all possible $(\text{HPO}_3)_n$ molecules can be divided into two groups according as they have or have not an active HPO_3 unit in their structure.

From the differences in the behaviour of the materials investigated, it now appears that the basic groups of proteins can also be divided into categories according to their selective action on the various metaphosphoric acids. To explain the results so far obtained, it is sufficient to suppose that the gliadin contained a large proportion of groups having a specific attraction for the "active" metaphosphoric acids, while glutenin, though it may have contained a fair proportion of these, had a considerable number that were non-specific in their action. In this connection it is interesting to note that glutenin is reported to contain considerably more arginine in its make-up than gliadin. The suggestion that the guanidine nucleus is prominent among the non-specific groups is not unreasonable on general grounds, seeing that its reactions are decidedly different from those of other basic nitrogen groups. This idea receives support from some experiments with edestin. These are not reported here in detail, as we had insufficient material for a complete examination, but the measurement showed that the edestin was less selective than the glutenin. It is reported to contain more arginine.

It should be emphasised, however, that it cannot strictly be argued from the marked differences in selectivity found with these particular samples that all gliadins and glutenins are similarly differentiated. Thus, although the figures for the gluten fall between those for the gliadin and the glutenin, as would be expected, it must be borne in mind that the acid binding capacity of the flours varied from 3.52 to 4.82 milliequivalents per gram of nitrogen. Comparing these figures with those in row (5) of Table II, it will be seen that they nearly bridge the gap between those for the gliadin and the glutenin. It is very improbable that the gliadin/glutenin ratio varies between the limits that would be required if the figures given held good for all gliadins and glutenins, and much more likely that their acid binding capacity is subject to some variation according to their source. As, however, the gliadin was prepared from the gluten, it is probable that the figures for gliadin and glutenin prepared from the same gluten will be found to bear to one another the general relationship shown in Table III.

Before discussing the figures in row (6) of Table II., mention should be made of experiments carried out with glacial phosphoric acid at other concentrations besides 0.1*N*. In dealing with separated proteins, this concentration has not the special advantage noted in the case of flour, but is nevertheless convenient, since stronger solutions hydrolyse more rapidly, while larger volumes of liquid must be used to get equivalent accuracy with weaker solutions. The experiments summarised in Table III. show

TABLE III.—UPTAKE OF GLACIAL PHOSPHORIC ACID BY GLUTEN FROM SOLUTIONS OF DIFFERENT CONCENTRATIONS IN MILLIEQUIVALENTS PER GRAM OF NITROGEN.

Concentration of acid (N)	0.02	0.04	0.10	0.20	0.40	1.0
Weight of gluten (gm.)	3	3	3	6	6	9
Volume of acid added (m.e.)	500	250	100	100	50	30
Volume titrated (ml.)	100	50	20	10	5	2
Uptake from titre to p_H 4.5 with NaOH	3.60	3.59	3.93	3.98	4.04	3.90
Uptake from titre to p_H 9.5 with NaOH	4.08	4.10	4.31	4.38	4.41	4.22

how little the uptake depends on the strength of the acid used, though there is a slight increase with increasing concentrations up to 0.4N. Thereafter it falls a little, presumably because any real increase there may have been in the uptake of acid was more than offset by the effect of water binding. At 0.1N water binding presumably made only about one-tenth the apparent negative contribution to the measured uptake, and so can be neglected.

In the experiments of Table II., one gram of protein was added to 40 ml. of 0.1N acid, while in those of Table III., 1.2 gram was added per 40 ml., and proportionally more or less according to the strength of the acid, so that approximately the same fraction of the acid was removed in each case. Table IV. shows how the uptake per gram of nitrogen varies

TABLE IV.—UPTAKE OF GLACIAL PHOSPHORIC ACID BY DIFFERENT WEIGHTS OF GLUTEN ADDED TO 0.1N ACID.

Weight of gluten added to 60 ml. acid	1.0	1.5	2.0	3.0	4.0
Uptake per gram N from titre to p_H 4.5 NaOH	3.86	3.89	3.86	3.72	3.68
Uptake per gram N from titre to p_H 9.5 NaOH	4.39	4.34	4.30	4.15	4.03

with the weight of gluten added to 60 ml. of 0.1N acid. It will be seen that as far as 2 gm. in 60 ml. (i.e. 1.33 gm. in 40 ml.) the variation in the measured uptake is within experimental error. At this point the titre to p_H 4.5 has been reduced about one-third, and that to p_H 9.5 by one-quarter. 8 gm. of even the most reactive flour added to 40 ml. of 0.1N acid would not over-pass this limit.

The figures in row (6) of Table II. refer to determinations made with trichloroacetic acid. As already noted, this acid is taken up by proteins in ever-increasing amounts, with rise in concentration above about 0.1N, but from 0.05N down to such low concentrations that precipitation is no longer complete (which varies with the protein) the uptake is substantially constant. This being a very strongly dissociated monobasic acid, it seems reasonable to assume that all the hydrions removed from these dilute solutions combine directly with the protein, and that a measure is obtained in this way of the true hydrion binding power of the protein. The differences between corresponding figures in rows (2) and (3) are a measure of the weakly dissociating hydrions removed from solution in combination with polybasic anions, one or more hydrions of which, being strongly dissociating, have combined with the protein. The differences between row (3) and row (6) further show that some fairly strongly dissociating hydrions are also removed from the solution, in addition to those combined directly with the proteins which are presumably the same in amount whatever acid is used, provided the p_H is low enough. Whereas the glutenin took up more polybasic anions with weakly dissociating hydrions attached, the gluten took up more with additional strongly dissociating hydrions—a

further indication of differential selective action. It is proposed to discuss these and other observations in their bearing on the molecular structure of the metaphosphoric acids more fully in another paper.

A comparison of row (5) with row (6) shows that for the gluten the number of hydrions, both weakly and strongly dissociating, taken up in association with polybasic metaphosphate anions is about one-quarter of the total, the remaining three-quarters being combined directly with the proteins. From the number of hydrions directly combined, it is easy to calculate that only one in every twenty-two nitrogen atoms in the gluten was able to co-ordinate a hydrion. It should be added that this statement is based on the additional information that the p_H of the gluten was close to p_H 6, which was found by Loeb's ferrocyanide method to be the lowest p_H at which the material could be freed of anions. The acid uptake was thus substantially the acid binding power. Thus, when the acid used for the measurement is glacial phosphoric, the acid bound is some 30 per cent. in excess of the hydrions bound direct to the protein.

The p_H of the Uncombined Proteins.

Measurements by Loeb's method on the gliadin and glutenin indicated that here also the figures in the table are substantially the acid binding capacities. The minimum p_H for washing out anions was observed to be p_H 5.5 for the glutenin, and p_H 6.85 for the gliadin. The value for glutenin is in agreement with those previously reported by Kondo⁹ and his co-workers. That for gliadin is close to the value p_H 6.5 given by Csonka, Murphy and Jones,¹⁰ but quite different from p_H 5.1 recently reported by Kemp and Rideal.¹¹ For our purpose we need the p_H at which the protein is uncombined, and Loeb's method is a very direct way of determining this. This p_H has a definite value, even for a mixture of proteins which separately give different p_H 's for no combination, for, as Bungenberg de Jong¹² has pointed out, the proteins may be regarded as combined with each other between these p_H values. From the standpoint of the zwitterion theory, this combination merely means a balancing of the electric changes of oppositely charged proteins without the necessity for the presence of other ions. It has generally been assumed that a material is isoelectric (*i.e.* it does not exhibit cataphoretic movement) when it is at the p_H at which it can be washed free of extraneous ions.

Summary.

Making use of the fact that glacial phosphoric acid is a protein precipitant, measurements have been made of the capacity of the proteins of wheat flour to bind this acid by shaking them up with an excess of the acid and determining the amount remaining in solution by back titration on an aliquot.

Solutions of potassium chloride, hydrochloric acid and trichloroacetic acid are slightly diluted by shaking with wheat starch, but there is no appreciable change in the concentration of a solution containing about 8 gm. of glacial phosphoric acid per litre, owing to the balancing of a very small uptake of acid by a "binding" of some water by the starch. The

⁹ K. Kondo and T. Hayashi, *Mem. Coll. Agric. Kyoto Imp. Univ.*, 1931, 11, 1.
K. Kondo, M. Murayama, and M. Iwamae, *J. Chem. Soc. Japan*, 1933, 84, 904.

¹⁰ F. A. Csonka, J. C. Murphy, and D. B. Jones, *J. Amer. Chem. Soc.*, 1926, 48, 763.

¹¹ I. Kemp and E. K. Rideal, *Proc. Roy. Soc.*, 1934, 147A, 11. In a paper shortly appearing Kemp states that the gliadin used by Kemp and Rideal had been denatured by long contact with alcohol, and gives a value of p_H 5.92 \pm 0.005 for the isoelectric point of the native protein which is in substantial agreement with ours.

¹² H. L. Bungenberg de Jong, *Trans. Faraday Soc.*, 1932, 28, 798.

concentration change caused by adding flour is therefore due to acid taken up by the protein.

The capacity of thirty-seven flours to bind glacial phosphoric acid varied from 6.7 to 10.1 milliequivalents per 100 gm. of flour. The uptake tended to be greater for the flours of higher nitrogen content, but the acid bound per gram of nitrogen varied from 3.52 to 4.82.

Although electrometric titrations revealed differences in the proportions of the constituent metaphosphoric acids in different batches of glacial phosphoric acid, determinations of the binding capacity of a gluten with eight different solutions gave a variation of only 5 per cent. between the highest and lowest values.

The uptake per gram of a gluten varied only slightly with the concentration of the acid between 0.02 and 1.0 normal, and was independent of the amount of gluten added, provided not more than a quarter of the acid was removed from the solution. In confirmation of a theory of the molecular structure of the metaphosphoric acids, put forward in an earlier paper, it has been found that protein removes certain metaphosphate ions from solution in preference to others. It has further been found that different proteins are selective to different degrees, showing that their basic groups can be differentiated as regards their action on glacial phosphoric acid.

Reasons are given for thinking that the uptake of trichloroacetic acid by gluten from a 0.5*N* solution is a measure of its hydrion binding capacity; if so, the additional titratable acid bound (roughly 30 per cent.) when glacial phosphoric acid is used, must be in the form of hydrions associated with polybasic anions.

The lowest p_H at which the materials could be washed free of anions (the isoelectric point) was found by Loeb's ferrocyanide method to be: the gluten — p_H 6.1, the gliadin — p_H 6.85, the glutenin — p_H 5.5, and one of the flours p_H 5.95. The p_H values were in each case close to those of the materials as procured, and a correction of a few per cent. only had to be applied to the acid uptake to obtain the acid binding capacity.

Our thanks are due to Dr. E. A. Fisher and Dr. P. Halton of the Research Association of British Flour Millers for supplying the flours used in this investigation and for giving information regarding them.

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THE TEMPERATURE COEFFICIENT OF THE SOLUBILITY OF HYDROGEN IN ORGANIC SOLVENTS.

BY E. B. MAXTED AND C. H. MOON.

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While the variation with temperature of the solubility of hydrogen in the organic solvents commonly used in catalytic hydrogenation is of considerable importance in the analysis of the factors which control the temperature coefficient of hydrogenation reactions in liquid systems, little has been published on the magnitude and direction of this variation for the common hydrogenation solvents, *e.g.* acetic acid and ethyl alcohol, over a reasonably extensive range of temperature.

Earlier work ¹ indicates that, in general, the variation of solubility with temperature is positive; but (save for benzene, which was studied by Horiuti, and alcohol, for which solubility values between 0° and 19° were measured by Timojew) measurements are available, for the solvents now investigated, only at 20° and 25°.

In the present work, solubility determinations have been made for acetic acid, ethyl alcohol, ethyl acetate, chloroform and benzene, over a wide temperature range. The data obtained are expressed in the form of the Bunsen solubility coefficient, namely as the volume of hydrogen, reduced to N.T.P., which, at the temperature of the measurement, is dissolved by one volume of the solvent when the partial pressure of the gas is 760 mm. This coefficient, α , bears a relationship to the Ostwald coefficient, used by Just, Christoff and Horiuti, of the form:

$$\alpha = \frac{273}{T} \gamma$$

in which T is the absolute temperature and γ the Ostwald coefficient, *i.e.* the ratio of the concentration of the hydrogen in the liquid phase to its concentration in the gas phase. Each of these coefficients requires a knowledge, firstly, of the coefficient of dilatation of the liquid studied, (in the case of a gas of low solubility, dilatation due to the dissolved gas is negligible) and, secondly, of the vapour pressure of the solvent at the temperature of the determination. The operation of the Henry-Dalton law is assumed, since, as Horiuti has pointed out, any deviations from this are likely to be small under the conditions of the measurement and data are not available for applying this possible small correction.

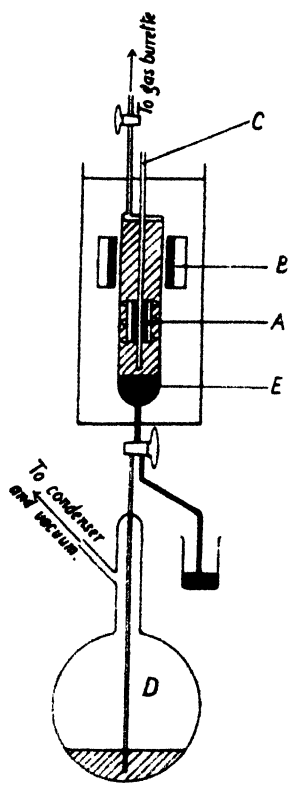


FIG. 1.

Experimental.

A considerable amount of preliminary work was carried out in order to determine suitable apparatus and general technique. The apparatus employed by Just consisted of an absorption vessel, which was connected with a gas-measuring system and shaken. Horiuti used a magnetically operated stirrer in place

of shaking the absorption vessel.

At the beginning of the present work, Horiuti's apparatus, with the exception of a small modification in the gas burette, was constructed and in general, was found to work very well; there appeared to be room for improvement only in minor points. The slight overheating of the liquid in the absorption pipette by the coil of the electromagnet operating the stirrer was minimised by making the coil a self-contained immersed unit of sufficient diameter to allow an annulus of the thermostatic liquid to interrupt direct contact between this coil and the glass wall of the absorption

¹ W. Timojew, *Z. physikal. Chem.*, 1890, 6, 141; G. Just, *ibid.*, 1901, 37, 342; A. Christoff, *ibid.*, 1917, 79, 456; J. Horiuti, *Inst. Chem. Physic. Research, Tokyo*, 1931, 17, 125.

pipette. This modification is shown in Fig. 1, in which A is the magnetically operated stirrer which is caused to rise and fall by interruption of the current flowing through the coil, B. The stirrer was of glass, of annular form, sealed over a short length of soft iron tubing and was provided with external glass fins, as shown. An internal thermometer pocket, C, acted as a vertical axis and guide for the stirrer. The diagram also shows the general arrangement adopted for degassing,² the liquid being boiled under reduced pressure in the flask, D. The portion of the degassed liquid taken for the solubility measurement was sealed from the remainder by a mercury cushion, E; and its volume was determined by weighing. Some measurements carried out with this apparatus are included in the section dealing with solubility in acetic acid.

For efficient stirring, however, including the provision of conditions such that the surface of the liquid in the pipette was broken by the stirrer, the free gas space above the solvent had, for mechanical reasons, necessarily to be of a greater volume than is conducive to accuracy in measuring the gas absorption: otherwise, with less vigorous stirring, the time of attain-

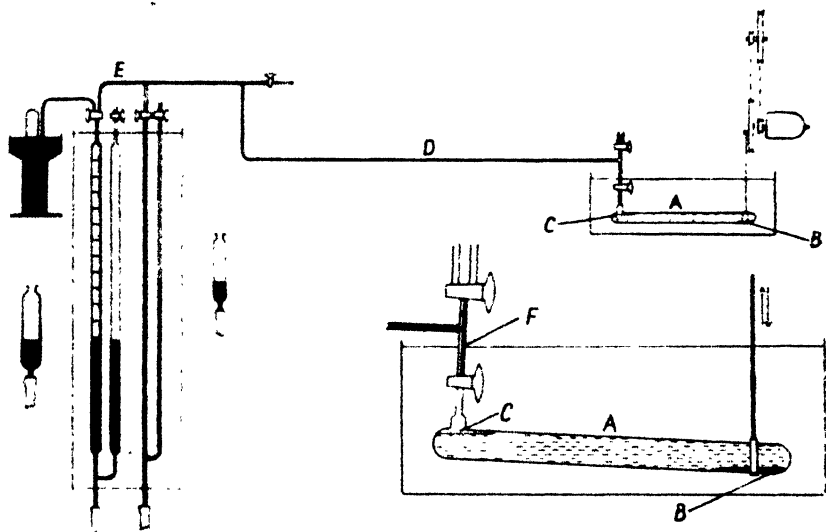


FIG. 2.

ment of equilibrium became rather prolonged. As an alternative to magnetic stirring, agitation of the absorption vessel itself, as in Just's method, was tried, the vessel being connected with the gas burette by a capillary connection. This avoided local overheating; but there is a tendency towards the formation of liquid threads in the connecting capillary, with consequent obstruction of accurate reading.

The apparatus finally adopted is illustrated in Fig. 2. The gas space above the solvent was reduced to a minimum by employing a solution vessel of the form shown at A. This vessel, which was immersed in a thermostat, contained, in addition to the solvent, a small quantity of mercury, B, and was rocked so that the mercury and the gas bubble, C, moved along the tube in opposite directions. This secured intimate contact of the gas with the whole of the previously degassed liquid, and led to a relatively rapid attainment of equilibrium.

The absorption vessel was connected by a long glass capillary link, D, approximately 1 metre in length, to a gas-measuring system, E, which was immersed in a glass-fronted tank maintained at a constant temperature.

² Cf. Horiuti, *loc. cit.*¹.

The smaller of the gas burettes was graduated in hundredths of a cubic centimetre.

The various solvents were already available in a high state of purity; and purified electrolytic hydrogen was used. Further purification by sorption in, and desorption from, palladium did not cause any measurable change in the observed solubility values.

In order to carry out a measurement, the absorption vessel was detached by cutting the connecting tube at the point, F. A small quantity of clean mercury was introduced, and the vessel was filled with solvent with the exception of the space C. The free absorption vessel, containing the solvent, was now immersed in warm water, in such a position that the gas space, C,

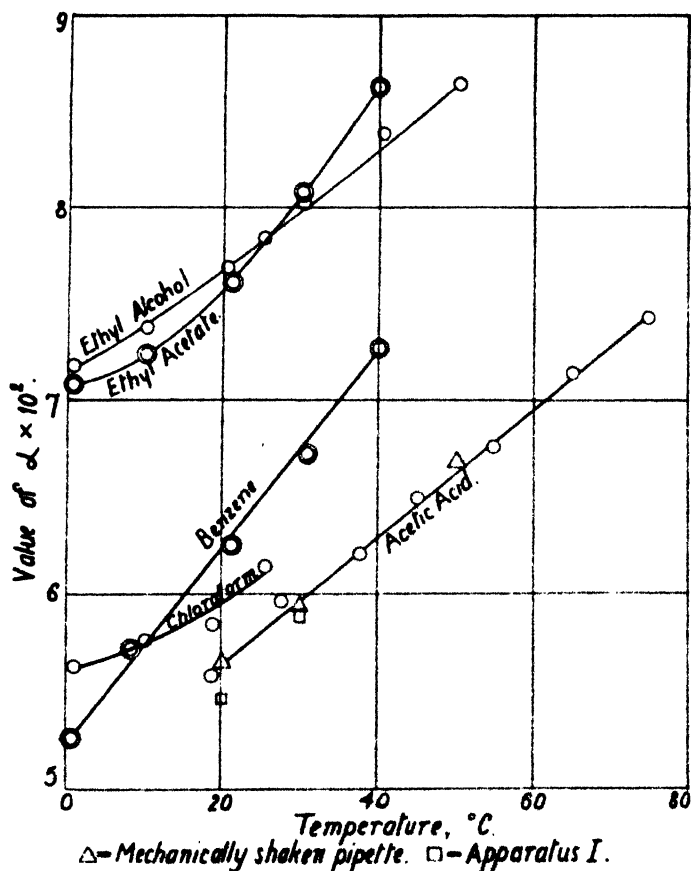


FIG. 3.

was uppermost, and degassing was carried out by prolonged boiling *in vacuo*. Since the obtaining of concordant maximum values for the solubility depends on the completeness of this degassing process, great care was taken with this stage. The elimination of dissolved gas was accelerated by periodically closing the tap and vigorously shaking the absorption vessel: further, the shape of the vessel was, in itself, conducive to the rapid and complete freeing of the liquid from dissolved gas, since the boiling took place from the bottom of, and throughout, the liquid, by reason of the small area available for surface evaporation; and the bubbles of solvent vapour thus traversed and scavenged the whole of the bulk of the liquid. The replacement of tap grease by, for instance, the

TABLE I.

Temperature. °C.	Weight of Liquid. Grams.	Density of Liquid at Solution Temperature.	Vapour Pressure in mm. Hg. of Liquid at Solution Temperature.	Volume Gas Dissolved. C.C. at N.T.P.	<i>a.</i>
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Hydrogen in Acetic Acid.

(a) Rocking Pipette.

18.6	122.64	1.0507	11.0	6.41	0.0558
27.4	111.49	1.0367	15.0	6.28	0.0596
37.5	113.71	1.031	30.0	6.565	0.0620
45.0	113.00	1.023	45.0	6.73	0.0649
54.9	114.34	1.011	72.0	6.915	0.0676
64.8	111.96	1.000	109.0	6.85	0.0714
74.8	115.41	0.989	166.0	6.765	0.0742

(b) Mechanically Shaken Pipette.

20.0	172.26	1.049	12.0	9.15	0.0566
30.0	141.95	1.030	21.0	7.89	0.0594
50.0	156.70	1.017	57.0	9.54	0.0669

(c) Magnetic Stirrer (Apparatus I).

20.0	137.22	1.049	12.0	7.13	0.0547
30.0	137.17	1.039	21.0	7.55	0.0590

Hydrogen in Ethyl Alcohol.

0.6	82.56	0.8063	12.2	7.235	0.0718
10.0	81.39	0.7978	23.8	7.285	0.0737
20.3	82.17	0.7890	44.0	7.545	0.0769
25.0	80.54	0.7851	60.0	7.405	0.0784
30.0	81.03	0.7808	78.0	7.52	0.0802
40.0	83.39	0.7730	133.0	7.48	0.0840
40.8	80.40	0.7720	140.0	7.13	0.0839
50.0	80.16	0.7633	220.0	6.45	0.0864

Hydrogen in Ethyl Acetate.

0.5	88.13	0.9244	25.0	6.69	0.0708
10.0	89.31	0.9126	42.7	6.53	0.0724
21.0	87.54	0.8993	76.9	6.66	0.0761
30.0	88.27	0.8883	118.7	6.76	0.0808
39.8	89.70	0.8762	184.0	6.70	0.0863

Hydrogen in Chloroform.

1.0	124.85	1.5260	61.0	4.44	0.0563
10.0	123.71	1.5050	100.0	3.90	0.0576
18.7	121.67	1.4886	149.6	3.83	0.0584
25.3	137.08	1.4750	197.0	4.224	0.0614

Hydrogen in Benzene.

0.5	89.31	0.9001	25.0	5.06	0.0526
8.3	88.01	0.8920	43.0	5.325	0.0572
21.2	89.68	0.8775	79.0	5.725	0.0625
30.6	90.93	0.8675	123.0	5.905	0.0672
40.0	90.44	0.8576	181.1	5.835	0.0727

mixture of phosphoric acid and caramelised glucose used by Horiuti, was found to be unnecessary if the tap was re-greased for each measurement.

The absorption vessel was now re-connected by fusion to the remainder of the apparatus and allowed to attain the temperature of the thermostat. The flexible capillary link, D, was next evacuated with a Hyvac pump, then filled with hydrogen from the large burette and re-evacuated, evacuation and filling being carried out from opposite ends of the link in order to avoid a cushion effect. Finally, the gas-measuring system was placed in connection with the degassed liquid. In the absence of rocking, solution was very slow—of the order of 0.01 c.c. per minute—and the position of the zero point could thus be determined accurately. The rocking mechanism was now started, and the absorption followed by means of the smaller burette.

Solubility of Hydrogen in Acetic Acid.—The solubility of hydrogen in this solvent was determined in three independent types of apparatus, namely by the rocking pipette method, as described above, in apparatus provided with a magnetic stirrer of the Horiuti type, and in a mechanically shaken absorption pipette. The results obtained by these three methods are summarised in Table I.

The concordance of the results obtained in Series *a* and *b*, which is most easily seen by reference to the collective graph, may be noted. The figures are, moreover, in good agreement with Just's previous determinations, $\alpha_{10} = 0.0575$ and $\alpha_{25} = 0.0580$. The values obtained in the apparatus provided with a magnetic stirrer were slightly lower than the above, probably for the reasons already discussed; and it is considered that the variation of solubility with temperature is most accurately given by the closely agreeing results of Series *a* and *b*.

Solubility in Ethyl Alcohol.—For this, and for the remaining solvents, the rocking pipette method was used throughout. The experimental results for the temperature range 0–50° are also contained in Table I.

Just's values $\alpha_{10} = 0.0804$ and $\alpha_{25} = 0.0819$ are slightly higher than the above figures; but the alcohol used by Just is stated to have been of 98.5 per cent. purity, whereas, in the present work, a pure specimen was employed.

Solubility in Ethyl Acetate.—Data relative to this are also contained in Table I. As before, previous data, due to Just, are only available for 20° and 25°. Just's value of α for the latter temperature (0.0780)

falls almost exactly on the above curve. His value for 20° (0.0734) is slightly lower.

Solubility in Chloroform.—The values obtained are given in Table I.

Solubility in Benzene.—In this case, previous data, due to Horiuti, are available for comparison, in addition to Just's figures for 20° and 25°.

If the results in Table I. are compared with Horiuti's figures and with those of Just, converted in each case into the form of the Bunsen coefficient, it will be seen that there is almost complete agreement with Horiuti's values but that Just's

figures are slightly higher. The comparison is shown in Table II.

TABLE II.

Author.	Temperature, °C.	Value of α .
Horiuti .	7.0	0.0571
	22.9	0.0646
	41.3	0.0733
Just .	20.0	0.0659
	25.0	0.0693

Summary.

The solubility of hydrogen in acetic acid, ethyl alcohol, ethyl acetate, chloroform and benzene has been determined over various ranges of temperature lying between 0° and 75°. In each case a positive temperature coefficient was observed.

The results have been examined critically in connection with the known solubility values at 20° and 25° and, in the case of benzene—for which solubility measurements have already been made up to about 60°—over a wider range. In general, where checking values are available, there is good agreement.

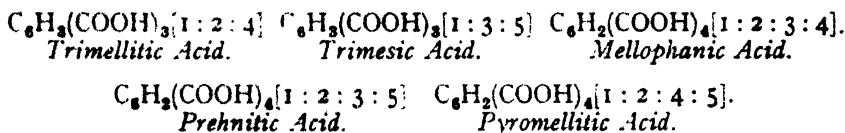
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THE DISSOCIATION CONSTANTS OF SOME POLYBASIC ACIDS.—PART II.

BY W. R. MAXWELL AND J. R. PARTINGTON.

Received 25th February, 1936.

The present communication deals with the acids :



These acids complete the series of acids formed by substituting hydrogen atoms in benzene by carboxyl groups, the other members having been, with the exception of terephthalic acid, described in Part I.¹ It has not been possible to determine the constants of this acid owing to its extremely slight solubility. The experimental method and the method of calculation used were the same as described in Part I., but it should be pointed out that the various expressions given for "u" on page 925 of Part I. are really expressions for "—u" and should therefore be multiplied by —1. This correction does not affect the validity of any of the formulæ or results given as expressions of the correct sign were actually used.

Preparation of Acids.

Trimellitic Acid.—Pure pseudo-cumene (B-pt. 169° C., 760 mm.) was first prepared from Kahlbaum's pseudo-cumene ("pure" B-pt., 160–170° C.) by conversion into the sulphonic acid, recrystallisation of the latter, and subsequent hydrolysis with superheated steam.² This was then oxidised with alkaline permanganate,³ and the acid obtained through the barium salt. It was recrystallised several times from conductivity water. M.-pt., 238° C.

Trimesic Acid was prepared by oxidation of mesitylene with alkaline permanganate.⁴ It was isolated through the barium salt and recrystallised several times from conductivity water. M.-pt., 368° C.

Mellophanic Acid.—Owing to some confusion in the literature as to the structure and melting-point of this substance it was thought desirable to prepare it by two different methods :

¹ Maxwell and Partington, *Trans. Faraday Soc.*, 1935, 31, 922.

² Jacobsen, *Lieb. Ann.*, 1877, 184, 199. Schultze, *Ber.*, 1909, 42, 3603.

³ Schultze, *Lieb. Ann.*, 1908, 359, 143.

⁴ Ullmann and Uzbachian, *Ber.*, 1903, 36, 1799.

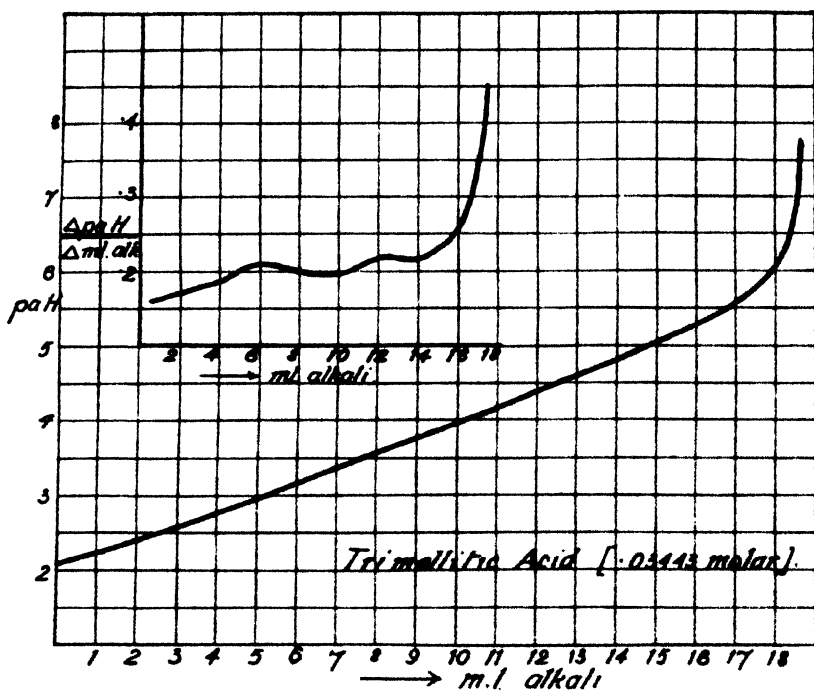
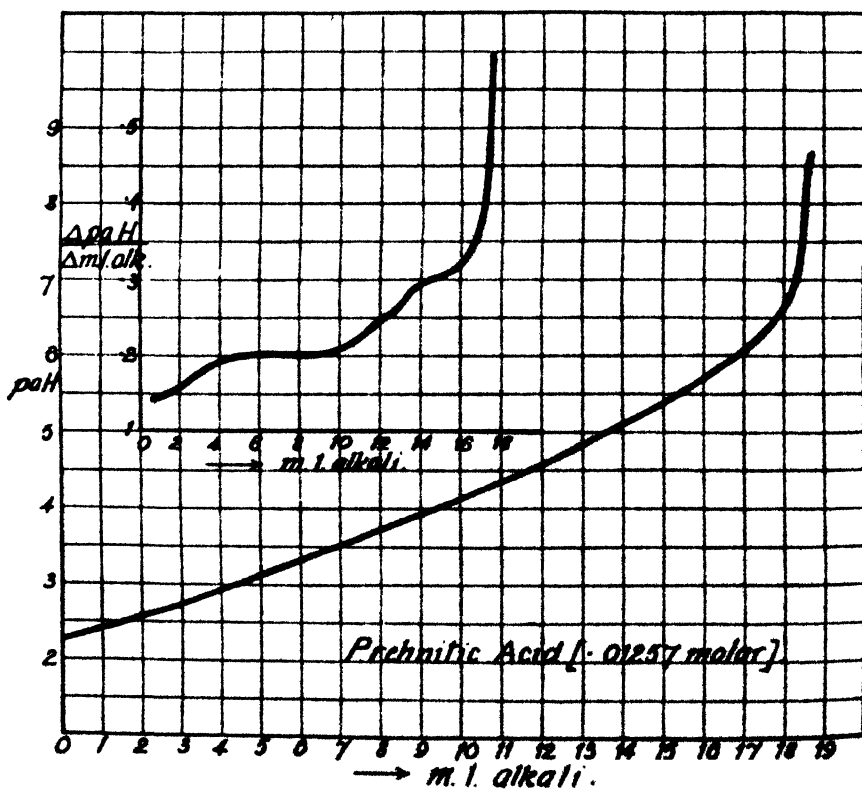


FIG. 1.



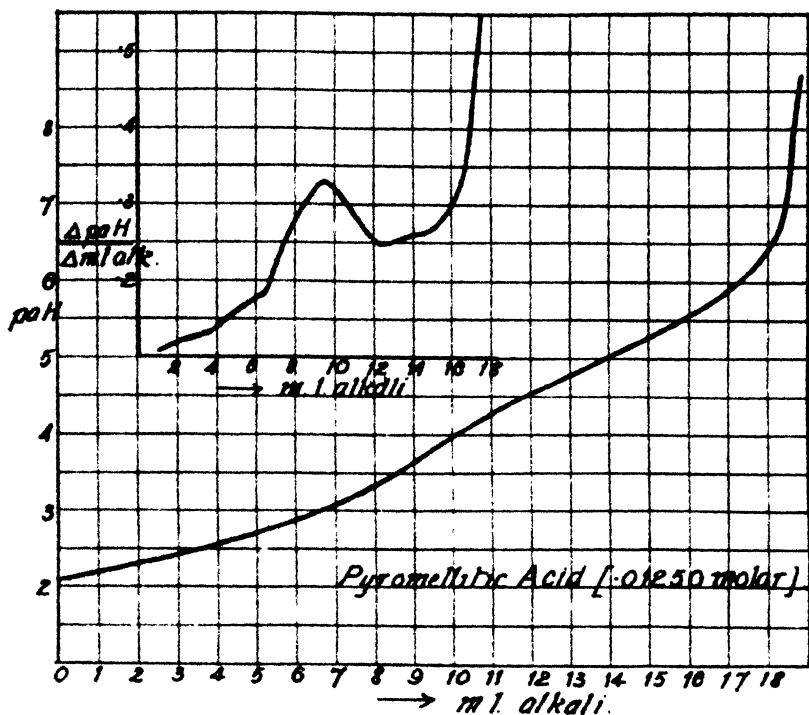


FIG. 3.

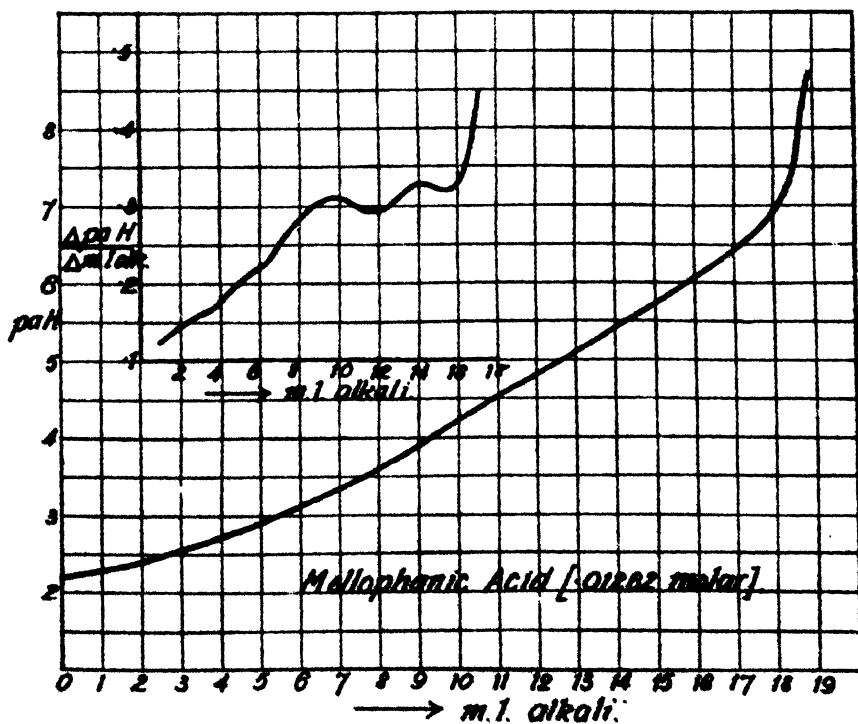


FIG. 4.

(a) Pentamethyl benzene was caused to undergo the Jacobsen reaction with concentrated sulphuric acid whereby hexamethyl benzene and 1 : 2 : 3 : 4 tetramethyl benzene sulphonic acid were obtained.⁵ The latter compound was isolated as the sodium salt and from this by treatment with concentrated sulphuric acid and superheated steam 1 : 2 : 3 : 4 tetramethyl benzene was obtained which was oxidised to the corresponding acid with alkaline permanganate.⁶ The acid was isolated through the barium salt and recrystallised several times from conductivity water. M.-pt., 244° C.

(b) 4 : 7-Dimethyl-2 : 2-diethylindan-1 : 3-dione was first prepared⁷ by condensing diethyl malonyl chloride with *p*-xylene in carbon disulphide solution in the presence of aluminium chloride. This was then oxidised with nitric acid in sealed tubes at 140° C. The benzene 1 : 2 : 3 : 4 tetra-

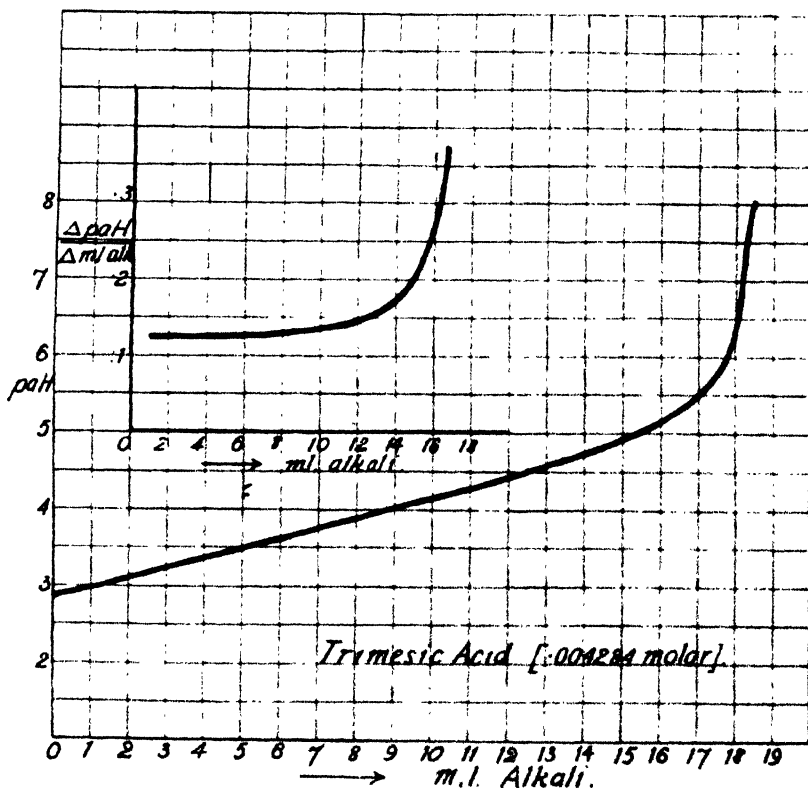


FIG. 5.

carboxylic acid isolated from the product was crystallised several times from concentrated nitric acid, heated in a vacuum for 8 hours at 160° C. over KOH, and finally recrystallised from conductivity water. M.-pt., 244° C.

Prehnitic Acid.—Mesitylene carboxylic acid⁸ was first prepared from bromomesitylene by Grignard's reaction, treatment with CO₂, and subsequent decomposition with ice and hydrochloric acid. This was then dissolved in sodium carbonate solution and oxidised to prehnitic acid with alkaline permanganate on the water bath, the oxidation being complete

⁵ Smith and Lux, *J. Amer. Chem. Soc.*, 1929, 51, 2997.

⁶ Töhl, *Ber.*, 1888, 21, 907.

⁷ Freund and Fleischer, *Lieb. Ann.*, 1915, 411, 14.

⁸ Bamford and Simonsen, *J. Chem. Soc.*, 1910, 97, 1904.

after about thirty hours. The acid was isolated through the barium salt and recrystallised several times from conductivity water. M.-pt., 263-266° C. Oxidation with dilute nitric acid in sealed tubes at 170-180° C.* gave a product which was difficult to purify.

Pyromellitic Acid.—Acetyl *pseudo*-cumene was first prepared from *pseudo*-cumene and acetyl chloride by the Friedel-Craft's reaction, and this was then oxidised first to durylic acid with sodium hypobromite,⁸ and then to pyromellitic acid with alkaline permanganate. The acid was isolated through the barium salt and recrystallised several times from conductivity water. M.-pt., 276° C.

Acids containing water of crystallisation were dehydrated by heating at 110° C. in a vacuum over phosphorus pentoxide before weighing out.

Remarks on the Titrations.

The titration of solutions of mellophanic acid prepared by both methods and at the same concentration of both acid and alkali gave the same results, thus showing them to be identical. Trimesic acid was titrated at one

TABLE I.

m.l. Alkali.	k_1 ($\times 10^3$).	k_2 ($\times 10^4$).	k_3 ($\times 10^5$).	k_4 ($\times 10^7$).	m.l. Alkali.	k_1 ($\times 10^3$).	k_2 ($\times 10^4$).	k_3 ($\times 10^5$).	k_4 ($\times 10^7$).
Trimellitic Acid (1). —(Acid = 0.03443 molar; alkali = 0.1116 molar.)					Mellophanic Acid (6). —(Acid = 0.006307 molar; alkali = 0.02745 molar.)				
0, 7, 14	2.68	1.51	7.73	—	0, 6, 10, 15	7.01	5.21	1.75	6.06
2, 8, 15	2.94	1.45	7.73	—	2, 7, 11, 16	7.42	5.11	1.74	6.13
4, 10, 16	2.97	1.45	7.79	—	4, 8, 12, 17	7.36	5.18	1.70	6.32
5, 11, 17	2.99	1.44	7.95	—	Prehnitic Acid (7). —(Acid = 0.01257 molar; alkali = 0.05467 molar.)				
Trimellitic Acid (2). —(Acid = 0.01721 molar; alkali = 0.05536 molar.)					0, 5, 10, 16	3.61	3.33	3.73	($\times 10^6$) 1.88
0, 8, 14	2.77	1.44	7.13	—	2, 6, 11, 17	3.94	3.09	3.88	1.93
2, 8, 17	2.97	1.41	7.06	—	3, 8, 12, 17	3.99	3.10	3.83	1.93
2, 10, 16	2.99	1.43	7.05	—	Prehnitic Acid (8). —(Acid = 0.006285 molar; alkali = 0.02767 molar.)				
4, 14, 17	3.01	1.40	7.05	—	0, 4, 10, 15	3.65	3.14	3.01	1.56
Trimellitic Acid (3). —(Acid = 0.008606 molar; alkali = 0.02796 molar.)					2, 6, 12, 16	4.00	2.85	3.27	1.54
0, 8, 14	2.59	1.29	5.67	—	3, 8, 12, 16	3.99	2.90	3.26	1.54
2, 9, 16	2.74	1.24	5.72	—	Pyromellitic Acid (9). —(Acid = 0.01250 molar; alkali = 0.05436 molar.)				
4, 9, 16	2.84	1.23	5.72	—		($\times 10^3$)	($\times 10^3$)		
4, 10, 17	2.81	1.25	5.96	—	0, 5, 10, 16	1.04	1.38	3.44	2.86
Trimesic Acid (4). —(Acid = 0.004284 molar; alkali = 0.01398 molar.)					2, 6, 11, 17	1.08	1.36	3.43	2.91
	($\times 10^4$)		($\times 10^4$)		4, 8, 12, 17	1.14	1.33	3.41	2.92
0, 7, 15	5.64	1.10	1.25	—	Pyromellitic Acid (10). —(Acid = 0.006250 molar; alkali = 0.02730 molar.)				
2, 9, 13	6.12	1.02	1.31	—		($\times 10^3$)			
4, 11, 16	6.17	1.05	1.22	—	0, 4, 10, 15	9.15	1.35	3.28	2.54
5, 9, 16	6.32	1.03	1.23	—	2, 6, 12, 16	9.32	1.34	3.27	2.62
Mellophanic Acid (5). —(Acid = 0.01262 molar; alkali = 0.05448 molar.)					3, 8, 12, 16	9.72	1.31	3.26	2.62
	($\times 10^3$)				Note. —The correct values of k are obtained by looking up the corresponding column. Thus for Pyromellitic Acid k_4 is ($\times 10^6$) and not ($\times 10^7$).				
0, 5, 10, 16	7.89	5.73	1.96	7.55					
2, 6, 12, 17	8.48	5.46	1.99	7.55					
3, 8, 13, 17	8.30	5.56	1.90	7.55					

* Mills, *J. Chem. Soc.*, 1912, 101, 2191.

TABLE II.

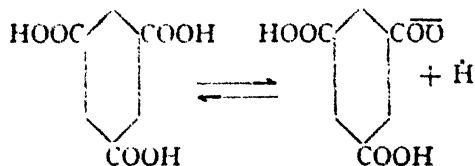
Titre.	E.M.F.	Titre.	E.M.F.	Titre.	E.M.F.	Titre.	E.M.F.	Titre.	E.M.F.
<i>Trimellitic Acid (I.).</i>									
0.00	.2421	5.98	.1779	11.00	.1178	15.00	.0662	18.36	— .0182
2.00	.2228	7.00	.1653	12.00	.1052	16.01	.0519	18.53	— .044
3.99	.2016	8.00	.1534	13.02	.0921	17.02	.0345	18.65	— .090
5.05	.1894	10.00	.1298	13.99	.0798	18.00	.0052		
<i>Trimellitic Acid (II.).</i>									
0.00	.2323	5.98	.1766	12.00	.1050	17.01	.0345	18.81	— .099
1.99	.2167	7.98	.1529	14.02	.0789	18.01	.0087		
4.00	.1983	9.99	.1298	15.98	.0518	18.61	— .033		
<i>Trimellitic Acid (III.).</i>									
0.00	.2210	5.99	.1706	9.98	.1240	15.97	.0439	18.50	— .048
1.98	.2075	7.98	.1480	11.97	.0991	17.03	.0256	18.61	— .072
3.96	.1912	9.04	.1353	13.98	.0720	18.00	— .0046		
<i>Trimesic Acid (IV.).</i>									
0.00	.1962	6.02	.1511	12.98	.0945	17.99	— .0156	—	—
2.02	.1812	7.01	.1436	15.02	.0731	18.22	— .066	—	—
3.97	.1665	9.00	.1281	16.01	.0593	18.35	— .099	—	—
4.98	.1590	10.97	.1121	16.99	.0393	18.42	— .108	—	—
<i>Mellophanic Acid (V.).</i>									
0.00	.2380	5.00	.1929	10.00	.1155	15.99	.0056	18.55	— .092
2.00	.2232	6.00	.1803	12.02	.0801	17.02	— .0158	18.74	— .132
2.99	.2142	8.03	.1511	12.98	.0631	18.04	— .0475	18.87	— .147
3.99	.2043	9.03	.1334	14.00	.0437	18.28	— .061		
<i>Mellophanic Acid (VI.).</i>									
0.00	.2254	6.03	.1738	11.02	.0922	16.01	— .0025	18.91	— .143
2.00	.2122	7.02	.1610	12.01	.0748	17.02	— .0235	19.10	— .155
2.99	.2044	8.00	.1465	14.02	.0364	18.02	— .055		
4.02	.1952	10.03	.1100	15.04	.0159	18.51	— .093		
<i>Prehnitic Acid (VII.).</i>									
0.00	.2308	4.99	.1809	10.00	.1206	14.02	.0615	18.35	— .0572
2.01	.2134	6.01	.1685	10.99	.1080	16.00	.0259	18.46	— .078
3.01	.2033	8.02	.1445	12.00	.0939	17.02	.0050	18.58	— .117
4.00	.1924	9.02	.1326	12.99	.0790	18.03	— .0306	18.70	— .146
<i>Prehnitic Acid (VIII.).</i>									
0.00	.2200	5.99	.1638	14.03	.0533	18.49	— .088	—	—
2.00	.2050	8.00	.1402	15.04	.0350	18.61	— .110	—	—
2.99	.1961	9.99	.1147	15.97	.0175	18.73	— .131	—	—
3.99	.1862	11.97	.0880	18.01	— .0396	18.85	— .144	—	—
<i>Pyromellitic Acid (IX.).</i>									
0.00	.2416	5.00	.2048	10.00	.1305	14.04	.0661	18.32	— .0398
2.03	.2287	6.01	.1946	11.04	.1118	16.02	.0346	18.48	— .062
3.00	.2215	8.03	.1676	11.99	.0967	17.00	.0153	18.64	— .113
4.00	.2138	9.00	.1502	13.00	.0818	18.01	— .0174	18.80	— .147
<i>Pyromellitic Acid (X.).</i>									
0.00	.2294	3.98	.2050	10.02	.1271	15.01	.0476	18.36	— .051
2.00	.2182	5.99	.1881	11.97	.0943	16.01	.0314	18.53	— .078
3.00	.2120	8.01	.1633	14.01	.0631	18.05	— .031		

concentration only, owing to the fact that, for solutions of higher concentration than that given, appreciable salting out of the acid occurred at the junction with the potassium chloride solution in the bridge, and solutions of lower concentration were not likely to give reproducible results. The curves obtained by plotting $\Delta p\text{aH}/\Delta \text{ml. alkali}$ against ml. alkali show a number of "humps" corresponding to the basicity of the acid except in the case of trimesic acid, the three constants of which are not greatly different in magnitude, and hence a more or less smooth curve results. The values of the constants calculated are given in Table I. (1-10), and the data necessary for their calculation in Table II. (I. to X.). The volume of acid solution used for each titration was 20.05 ml. in cases 1 and 2 and 20.02 ml. in cases 3-10.

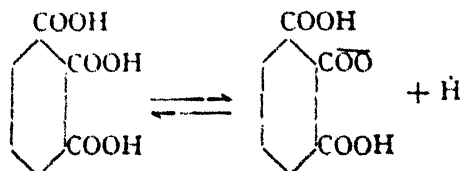
Discussion of Results.

The complete consequences which follow from the above results have not yet been worked out, but it appears that the promoting effect of unionised carboxyl groups is not, as had seemed possible from the results in Part I., simply a function of their number and distance apart. Thus, k_1 for benzene 1 : 2 : 4 tricarboxylic acid is about twice as great as k_1 for benzene 1 : 2 : 3 tricarboxylic acid in which the groups are closer together, and similarly: k_1 for pyromellitic acid is greater than k_1 for mellophanic acid where again the groups are closer together.

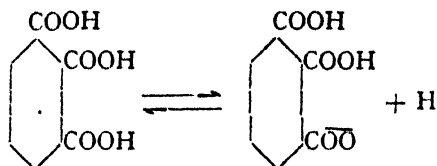
The values of the last dissociation constants are, however, in agreement with the hypothesis that the negative charge or charges on a dissociating ion produce an inhibiting effect which is a simple function of their number and distance from the dissociating carboxyl group. Two small deviations from this rule which arise when k_4 for prehnitic acid is compared with k_3 for hemi-mellitic acid, and k_3 for trimellitic acid is compared with k_2 for phthalic acid, are probably accounted for by deviations from the laws of ideal electrolytes. It should be pointed out that in drawing conclusions from the above results, and those in Part I., it must be remembered that in all except a few cases where the carboxyls in the dissociating molecule or ion occupy equivalent positions, the constants do not represent a simple equilibrium. Thus, for example, the first stage of ionisation of trimesic acid, whose carboxyls occupy equivalent positions, can occur in only one way (I.), but that of hemi-mellitic acid, in which the carboxyls are not all in equivalent positions, can occur in two ways (II.a and II.b), so that k_1 for the latter acid involves two different constants:



I.



II.a



II.b

It is hoped to discuss the results in more detail in a later paper.

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THE SYSTEM LAURIC ACID—SODIUM HYDROXIDE—WATER.

BY C. R. BURY AND R. D. J. OWENS.

Received 26th February, 1936.

This is a continuation of previous work¹ on systems of the type $XOH-MOH-H_2O$ (where XOH is a fatty acid, and M a metal), the object being to trace the changes that occur as the number of carbon atoms in the fatty acid changes, and as the nature of the metal is changed. Data for the system lauric acid—sodium hydroxide—water at 25° C. are presented here.

Experimental.

The general method of procedure was to mix lauric acid and a solution of sodium hydroxide of suitable concentration in a resistance glass tube, which was evacuated to avoid frothing, and sealed off. The tube was heated to 100° to ensure complete interaction of its contents, a homogeneous solution being generally obtained, and then shaken in a thermostat at 25° for periods up to eight weeks. The contents of the tube were filtered through a sintered glass filter-funnel, the operation being performed in the thermostat and in an atmosphere of nitrogen, and the liquid and moist solid analysed.

Modifications of this procedure were frequently necessary. Neutral or slightly alkaline solutions set on cooling to an opaque gel—the wet curd—that shows numerous hair-like strands of fibre—the curd—under the microscope. The wet curd is unsuitable for phase rule work as it can only be separated with difficulty into solution and moist solid. This difficulty was obviated by a process of artificial ageing. The wet curd was alternately cooled in tap water and heated in the thermostat for periods up to a month, being frequently broken up by vigorous shaking. In this ageing process it is essential that the mixture should never be heated above the temperature at which it is desired to establish equilibrium. As a result of this treatment the gel undergoes syneresis and the fibre strands become relatively short and collect in clumps, but do not appear to be otherwise,

¹ *Trans. Faraday Soc.*, 1935, **31**, 480.

changed, and can now readily be separated from the solution by filtration. Before this, however, the mixtures were shaken in the thermostat to ensure the establishment of equilibrium.

Lauric acid does not react completely with strong alkali even on heating to 100° and after continuous shaking for long periods. Apparently sodium laurate is so insoluble in strong alkali that it can act as a protective coating to the underlying acid. In studying equilibria involving strong alkali it is necessary to dissolve the lauric acid in weak alkali and then to add more sodium hydroxide.

Mixtures composed of dilute soap solutions with slight excess acid form colloidal suspensions of acid soap. The colloidal particles do not settle out completely on long standing, nor can they be separated from the mother liquor by any ordinary filter. Ultrafiltration had to be employed for these mixtures, a collodion membrane being used.

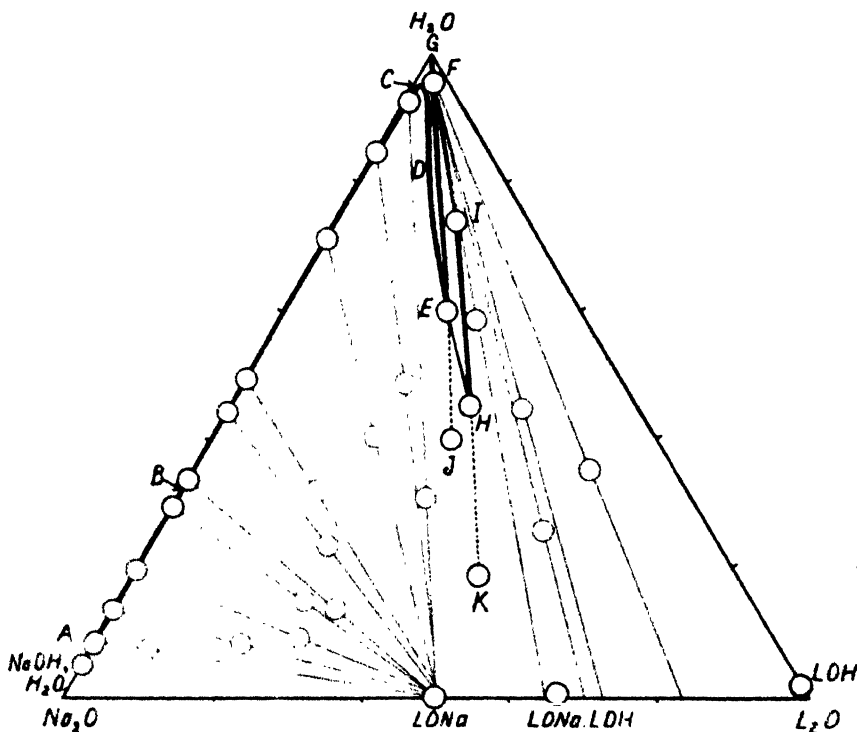


FIG. 1.

Mixtures composed of more concentrated soap solutions with excess acid separate on cooling into two liquid layers, a less dense layer of anisotropic liquid (liquid crystalline phase) and a denser layer of isotropic liquid (ordinary solution phase). Shaking forms an emulsion of the liquid crystalline phase in the ordinary solution phase which only settles out with extreme slowness. Pure samples of the lower layer can be obtained with ease, but it is impossible to get pure samples of the upper layer in reasonable time. Since the upper layer is "a phase of variable composition" it is impossible to deduce its composition by extrapolation of the tie lines in the usual manner. If the homogeneous mixture obtained on heating is placed in the thermostat and allowed to stand without shaking for a week or two, separation of the layers is much more complete. Analyses of the lower layers lie on the same curve as those of mixtures that have been shaken,

indicating that equilibrium has been established. Analyses of the upper layer of these unshaken mixtures (indicated in Table I. by the letters "ns.") give a fair idea of the composition of the liquid crystalline phase, though most of the samples contained a little of the lower layer.

Lauric acid was purified by two fractional distillations of its methyl ester. Solutions and moist solids were analysed by (a) estimating excess alkali (or acid) by titration with standard acid (or alkali), acidic moist solids being titrated in 10 per cent. alcoholic solution, and (b) estimating the total lauric acid by precipitation with hydrochloric acid, the acid being collected, washed, and then titrated with standard alkali in 20 per cent. alcoholic solution. Phenolphthalein was used as indicator.²

Lauric anhydride (L_2O), sodium oxide (Na_2O), and water were chosen as the components of the system, since any other choice would involve negative concentrations. Analyses of the solutions and of the moist solids in equilibrium with them, expressed in terms of these components, are given in Table I. All analyses quoted are the mean of two concordant deter-

TABLE I.

Solution.		"Moist Solid."				Solution.		"Moist Solid."			
Na_2O .	L_2O .	Na_2O .	L_2O .			Na_2O .	L_2O .	Na_2O .	L_2O .		
%.	%.	%.	%.			%.	%.	%.	%.		
40.56	0.00	—	—	NaOH, H_2O NaOH, H_2O + LONa.		0.77	5.20	3.74	23.85		
40.44	0.01	48.11	0.94			1.06	6.50	—	—		
						1.02	7.10	2.69	17.52	Curd	
39.40	0.02	33.71	18.96	LONa.		1.13	7.76	2.15	14.08		
34.65	0.06	25.11	40.20			1.47	10.64	—	—		
28.32	0.02	21.97	37.32			1.44	10.75	2.22	15.47		
24.43	0.03	20.07	35.21			0.03	0.22	1.22	30.04	Acid soap.	
20.06	0.03	16.63	43.02			0.07	0.40	1.57	24.93		
12.87	0.03	13.13	33.65			0.08	0.52	2.92	42.15		
10.82	0.03	12.16	39.40			0.09	0.68	1.31	14.40		
10.57	0.01	11.59	27.94			0.10	1.00	—	—		
7.21	0.03	9.07	25.20			0.20	1.30	—	—		
5.93	0.03	7.33	16.32			0.25	1.83	0.74 (ns.)	7.71	Liquid crystal.	
2.44	0.05	4.57	16.18	Curd.		0.30	2.62	—	—		
2.42	0.04	4.84	18.66			0.48	3.52	0.87	7.92		
1.47	0.08	3.22	12.06			0.48	3.55	1.41 (ns.)	13.39		
1.14	0.09	3.52	17.77			0.50	4.15	1.19 (ns.)	10.47		
1.08	0.07	3.08	14.17			0.90	6.72	1.77 (ns.)	15.23		
0.44	0.34	3.89	22.02			1.25	7.98	1.75	10.30		
0.44	0.31	4.77	27.63			1.30	10.15	2.27 (ns.)	21.23		
0.24	0.42	1.83	10.56			1.39	11.26	2.21	19.84		
0.28	1.45	—	—			1.60	12.10	2.08 (ns.)	17.79		
0.31	1.56	—	—			1.65	12.68	1.95	16.20		
0.39	2.31	3.68	22.61			1.78	13.67	2.08	17.25		
0.47	2.39	—	—			1.89	14.48	2.38 (ns.)	21.20		
0.54	2.89	4.98	30.21			2.00	15.26	2.44 (ns.)	21.59		
0.53	3.10	3.16	19.25			2.40	17.99	4.43 (ns.)	43.93		
0.57	3.75	4.13	25.85			2.66	19.63	3.46 (ns.)	38.40		
0.67	4.07	4.49	27.38			3.15	22.81	6.75 (ns.)	47.83		
0.74	4.92	3.72	23.74								

minations. In order to illustrate the most important points, these results are illustrated in the figure, in which triangular co-ordinates are used, and concentrations are expressed as mol. fractions except that an arbitrary value of 1000 has been taken for the molecular weight of water, following the device of McBain.

² McBain and Hay, *J. Chem. Soc.*, 1929, 589.

Discussion.

The solid phases in equilibrium with solutions on the alkaline side are (1) sodium hydroxide monohydrate, (2) anhydrous sodium laurate, and (3) curd. Anhydrous sodium laurate is the stable phase in contact with concentrated solutions of alkali containing practically no soap, represented on the diagram by the line BA, the point A representing a saturated solution of sodium hydroxide. Curd is stable in contact with less strongly alkaline, neutral, and even slightly acid solutions represented in the diagram by the line BCDE. The change of phase at the point B was detected by a change in the direction of the tie lines, but more clearly by the change in appearance of the solid phase. (This change of direction of the tie lines is not apparent in the figure owing to the method of plotting adopted; the points representing anhydrous sodium laurate and sodium laurate monohydrate are too close for separate representation.) The anhydrous salt usually appeared under the microscope to consist of broken fragments that showed no external sign of crystalline form, though a few observations suggested that it crystallised in thin plates. The curd appears as a mass of matted fibres. A series of experiments, not recorded in Table I., fixed the triple point B between the limits 11.3-12.8 per cent. Na_2O . Curd is a form of sodium laurate, but owing to the relative positions in the diagram of the line BCDE and the points representing sodium laurate and its possible hydrates, our analyses do not throw much light on its degree of hydration. Tie lines from points on the curve near B indicate that it does not contain more than one molecule water of crystallisation, while tie lines from the section CDE are quite indecisive. Experiments of McBain and his collaborators indicate a higher degree of hydration for soap curds, but it is possible that the degree of hydration depends on their treatment and on the solution with which they are in contact.³

The profound influence of a slight excess of acid or alkali on the solubility of sodium laurate in the neutral region CDE is shown by the figures given in Table II., which have been obtained by recalculation of figures given in Table I. The compositions of nearly neutral solutions saturated with respect to curd are expressed in grams soap (LONa), and excess acid (LOH) or alkali (NaOH) per 100 grams solution.

As is well known, sodium chloride and other salts lower the solubility of soaps in the same way; this being probably the first known example of the phenomenon of "salting out." The raising of the solubility by excess acid is, however, unexpected; since lauric acid is a weak acid its effect should be negligible except for a small secondary effect in repressing hydrolysis and thus removing from solution the small amount of free alkali that is normally present. The phenomenon appears to be analogous to the Krafft effect.⁴ In each case there is a sudden rapid increase in solubility; in the Krafft effect this is caused by a small increase in temperature, here by a small change in

TABLE II.

Per Cent.	Per Cent.
LONa.	Excess NaOH.
3.60	0.04
2.78	0.10
0.49	0.22
0.09	1.43
0.05	3.12
LONa.	Excess LOH.
5.4	0.47
7.7	0.88
10.5	1.80

³ McBain and Salmon, *J. Chem. Soc.*, 1921, 119, 1374; McBain, Lazarus and Pitter, *Z. physik. Chem.*, 1930, 147A, 87.

⁴ Krafft and Wiglow, *Ber.*, 1895, 28, 2566.

the other components of the solution. Before drawing any conclusions, however, it is desirable to investigate the system at other temperatures, and to ascertain whether the two phenomena have a common basis.

The effect of the repression of the solubility by alkali is to limit the area which represents the solution phase in the diagram to two narrow strips; one GA lying along the side of the triangle and representing solutions containing sodium hydroxide (0.40-6 per cent.), but practically no soap, the other GE lying along the neutral line and representing solutions containing soap (0.11-5 per cent.) with little excess acid or alkali.

As might be expected, lauric acid is practically insoluble in water and in dilute solutions of soap, but it dissolves appreciably in more concentrated solutions, as is shown in Table III. This seems only an example of a general phenomenon: Smith⁵ has pointed out that concentrated solutions of soap dissolve appreciable quantities of organic compounds of the most varied types, and makes the reasonable suggestion that the soap micelle is capable of incorporating these organic substances.

TABLE III.

LONa.	LOH.
Per Cent.	Per Cent.
1.14	0.12
6.67	1.35
9.35	2.21
17.20	3.34
24.60	3.74

The phases in equilibrium with the solution on the acid side are (1) lauric acid, (2) acid sodium laurate, and (3) a liquid crystalline phase. Lauric acid is in equilibrium with very dilute soap solutions (0 to about 0.1 per cent.); the co-existence of these phases is not indicated on the diagram. Acid soap is in equilibrium with a somewhat restricted range of more concentrated, but still dilute soap solutions (0.1-0.86 per cent.), represented in the diagram by the line FG. Analyses of moist solids indicate that its composition approximates to LONa, LOH, but that the ratio LONa:LOH increases as the concentration of soap in the solution in contact with it increases. It is impossible to draw any conclusions as to the degree of hydration from our analyses. Acid soap appears under the microscope to consist of very thin plates. It remains suspended in the mother liquor as a fairly stable colloidal suspension that exhibits well-marked striations on stirring, due to the plate-like form of the particles. The fact that acid soap forms these colloidal solutions suggests that it adsorbs sodium laurate from solution, and the variability of its composition is therefore not remarkable.

The liquid crystalline phase is in equilibrium with a wide range of slightly acid isotropic solutions (0.86-11.5 per cent. soap), represented in the diagram by the line EF. The compositions of the liquid crystals in equilibrium with these isotropic solutions are represented by the line HL. The equilibrium between these two phases can be followed into the region in which they are metastable with respect to formation of curd, as shown by the dotted lines EJ and HK. In general, compositions of liquid crystals approach those of isotropic solutions very closely, though the compositions of a particular liquid crystal and of the isotropic solution in equilibrium with it differ considerably. Study of these liquid crystals under the polarising microscope is much handicapped by the fact that they rapidly crystallise to acid soap at room temperature. Between crossed Nicols, the emulsion of liquid crystal in isotropic solution appears as a cloud of white circular discs—each covered by a similarly oriented black cross.

⁵ Smith, *J. Physic. Chem.*, 1932, **36**, 1401, 1672 and 2455.

The concentration of the ordinary solution at the triple point isotropic solution—liquid crystal—curd, represented by the point E, was not determined directly, since the treatment required to get a solution in equilibrium with curd and suitable for analysis is so different from that required for the liquid crystal. Solutions in equilibrium with liquid crystal, after being analysed, were inoculated with curd. This grew in a solution containing 1.65 per cent. Na_2O and 12.68 per cent. L_2O and in more concentrated solutions, but not in less concentrated solutions.

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A DIRECT DEMONSTRATION OF BOUND WATER IN GELATIN GEL.

BY EMIL HATSCHKEK.

Received 24th March, 1936.

When gelatin gels containing cobaltous chloride are allowed to dry at temperatures from 15° to 30° they turn a pure blue before all the water which they can lose at the latter temperature has evaporated. The water still remaining in the gel must therefore be considered as water bound by the gelatin in the sense that it is no longer free to hydrate the cobaltous chloride.

The quantitative determination of the amount thus bound seems of interest and offers no difficulty in principle. In practice it was found necessary to develop a technique by which gelatin films could be dried so as to have a uniform thickness, and therefore tint, and to remain flat until they had turned a pure blue. If free discs of gelatin gel a few mm. thick are allowed to dry in the usual way on gauze, the well-known complications arise: the rim dries more rapidly than the centre and thickens, and the discs bend into an anti-elastic surface, the colour of which is difficult to judge.

These complications are avoided, and flat discs are obtained, by casting the gel in circular frames, to which it adheres, in the following manner (Fig. 1): a polished metal plate A, the upper surface of which has been very lightly greased, is placed on a levelled table. A circular mould B, of hard wood, the lower face of which has been thinly coated with vaseline, is laid on the metal plate and weighted at the four corners. The periphery *bb* of the mould is varnished with shellac varnish; this does not destroy the adhesion of the gelatin but prevents its dehydration by the wood.

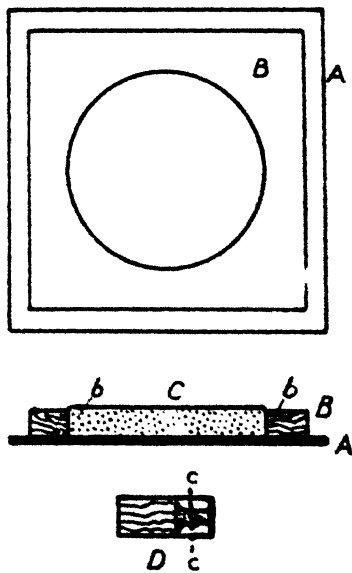


FIG. 1.

The mould is then filled with the gelatin sol C which is allowed to set for several hours or preferably overnight. When it has reached its full modulus or tensile strength the mould can be lifted off the metal plate by slowly tilting it; the disc of gel adheres to it and continues to do so during the drying process. The mould is hung up vertically, occasionally turned through 180° in its own plane, and the disc of gel allowed to dry until its colour is a pure blue. The change from an increasingly deep purple to pure blue is very sharp; if there is reason to suspect that the gel has been allowed to dry further than necessary, the discs can be placed in a moist atmosphere and allowed to take up water again until a purple tinge just begins to show.

To test how well defined the water content at the blue stage actually is, the following experiment was carried out. A specially thick disc was allowed to dry until the colour in transmitted daylight was judged to be a pure blue. It was removed from the mould in the manner to be described in the next paragraph and weighed; its weight was 3.342 gm. It was then placed in a moist atmosphere, carefully examined from time to time, and weighed when it showed an unmistakable purplish tinge. Its weight was then 3.365 gm., so that it had taken up 0.023 gm. of water. It was then dried to constant weight at 100° and left 2.510 gm. of dry residue, having lost 0.832 gm. of water compared with the original blue gel. The quantity of water—0.023 gm.—required to produce a marked change from pure blue according amounts to only 2.7 per cent. of the water content of the blue gel.

The discs dry to a fin round the periphery of the mould (see detail D) and are removed by cutting round the circle at *cc*. To determine the water content at the blue stage the discs are immediately placed in weighing bottles, weighed and then dried to constant weight at 100° , the temperature being raised very gradually so as to avoid melting.

If p_1 is the weight of the blue gel and p_2 that of the residue at 100° , $p_1 - p_2 = w$ is the weight of water in the blue gel. The dry residue consists of gelatin dried at 100° and anhydrous CoCl_2 in the ratio $g:c$, which can be calculated from the known quantities of gelatin and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ used in preparing the sol. The weight p_2 of gelatin in the dry residue is accordingly

$$p_2 = p_2 g / (g + c)$$

and the percentage of water in the blue gel H

$$H = 100w / (w + p_2).$$

Some authors define the gel by stating the weight h of water per gm. of dry gelatin which is

$$h = w / p_2.$$

Gelatin sols, the particulars of which are given below, were prepared from four different brands; the iso-electric gelatin was kindly supplied by Dr. Dorothy Jordan Lloyd. The sols usually contained 10 gm. of water per gm. of gelatin; although this low concentration prolongs the period of drying it permits the use of lower temperatures and makes it easier to obtain gels free from air bubbles. The relevant figures are as follows:—

(A) 10 gm. air-dry Nelson's "Transparent" gelatin + 5 gm. $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$. A sample of the gelatin dried at 100° gave 86.8 per cent. of dry matter. The ratio $g:c$ is therefore (as 1 gm. $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ gives 0.546 gm. CoCl_2):—

$$g/c = 8.68/2.730.$$

(B) 10 gm. gelatin from S. Combier, Annonay, dried at 100° , + 5 gm. $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$:—

$$g/c = 2.00/0.546.$$

(C) 10 gm. air-dry iso-electric gelatin + 5 gm. $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$. A sample dried at 100° gave 86.7 per cent. of dry matter:—

$$g/c = 8.67/2.730.$$

(D) 10 gm. Coignet "gold label" gelatin, dried at 100° + 5 gm. $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$:—

$$g/c = 2.00/0.546.$$

The results are as follows:

- (A) $p_1 = 2.143$ gm.; $p_2 = 1.538$ gm.; $w = 0.605$ gm.; $p_3 = 1.170$ gm.
 $H = 34.0$ per cent.; $h = 0.51$.
- (B) $p_1 = 2.590$ gm.; $p_2 = 1.850$ gm.; $w = 0.740$ gm.; $p_3 = 1.453$ gm.
 $H = 33.7$ per cent.; $h = 0.51$
- (C) $p_1 = 2.005$ gm.; $p_2 = 1.490$ gm.; $w = 0.515$ gm.; $p_3 = 1.132$ gm.
 $H = 31.4$ per cent.; $h = 0.43$
- (D) $p_1 = 1.840$ gm.; $p_2 = 1.375$ gm.; $w = 0.465$ gm.; $p_3 = 1.060$ gm.
 $H = 30.4$ per cent.; $h = 0.44$.

Discussion of Results.

Gelatin gels of different origin have been shown to contain between 30.4 and 34.0 per cent. of water which is not free to hydrate cobaltous chloride. These figures are in good agreement with the values for bound water found by entirely different methods. Thus T. Moran¹ finds: "... when the water content falls to 35.34 per cent. there is no separation of ice at any temperature. . . . This undoubtedly suggests that water is present in the gel in two states, which may be distinguished as 'bound' and 'interstitial' water. Bound water is merely water which is incapable of being frozen."

In the present investigation "bound" water is water which is incapable of hydrating cobaltous chloride and the agreement between the percentages of such water and Moran's values, while undoubtedly striking, must not be over-emphasised. Apart from other points Moran used an ash-free and iso-electric gelatin, whereas the gels described here contained cobaltous chloride, *i.e.* electrolyte in considerable amounts. It is almost certain that this affects the percentage of bound water, and there seems to be a possibility of obtaining a new insight into the effects of the Hofmeister series by investigating gels containing either cobaltous salts with different anions, or mixtures of cobaltous chloride with neutral salts of different anions. Work in these directions is in progress.

Summary.

Gelatin gels containing cobaltous chloride have been shown to contain from 30 to 34 per cent. of bound water incapable of hydrating the cobalt salt, a value in good agreement with the figures for bound water found by other methods.

¹ T. Moran, "The Freezing of Gelatin Gels," *Proc. Royal Soc.*, 1926, **112A**, 35.

THE MAGNETIC SUSCEPTIBILITY OF CHLORINE HEXOXIDE.

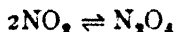
BY J. FARQUHARSON, C. F. GOODEVE AND F. D. RICHARDSON.

Received 23rd March, 1936.

A red oily liquid was detected by Bowen¹ in a study of the photochemistry of chlorine dioxide. The substance was isolated by Bodenstein, Hardeck and Padelt,² and was found by them to contain three atoms of oxygen to one of chlorine. Its molecular weight, when dissolved in carbon tetrachloride, was found to be 153.6, and it was called "chlorine hexoxide" (M.W. 167). Goodeve and Todd³ showed that in the gaseous state it existed entirely as ClO_3 , and this form was called "chlorine trioxide." It was with the object of determining the composition of the liquid and solid phases that the following investigation of the magnetic susceptibility was carried out.

It is a general rule that paramagnetism in molecules is associated with an unbalanced electronic structure. Any molecule with an odd number of circumnuclear electrons must be unbalanced, and therefore paramagnetic. This has been shown to be true for NO (15 circumnuclear electrons), NO_2 (23), and ClO_2 (33). It can be assumed that ClO_3 (41) will also be paramagnetic.

If a molecule with an odd number of electrons polymerises into a double molecule, the resulting polymer may be diamagnetic. For example, in the equilibrium



NO_2 is strongly paramagnetic, and N_2O_4 diamagnetic. It should be noted that molecules with an even number of electrons are not necessarily diamagnetic. The oxygen molecule, for example, is strongly paramagnetic by virtue of its being in a $^3\Sigma$ state. As a general rule, however, molecules with an even number of electrons are in a $^1\Sigma$ state, and are diamagnetic.

The fact that paramagnetic NO_2 polymerises to diamagnetic N_2O_4 has been used by Havens⁴ in order to arrive at the temperature variation of the susceptibility of NO_2 . He studied the magnetic susceptibilities of equilibrium mixtures of the two gases at different temperatures. The amount of N_2O_4 was determined from other data, and, allowing for its diamagnetism, the susceptibility of NO_2 was calculated. He found it to conform to Van Vleck's equation (see below). This equation has also been found to hold for chlorine dioxide.⁵

If chlorine trioxide polymerises to $^1\Sigma \text{Cl}_2\text{O}_6$ in the condensed state, the substance will be diamagnetic. If there is an equilibrium between the two molecular species there may be paramagnetism to a greater or

¹ E. J. Bowen, *J.C.S.*, 1923, 123, 2328; H. Booth and E. J. Bowen, *J.C.S.*, 1925, 127, 510.

² M. Bodenstein, P. Hardeck and E. Padelt, *Z. anorg. Chem.*, 1925, 147, 233.

³ C. F. Goodeve and F. A. Todd, *Nature*, 1933, 132, 514.

⁴ G. Havens, *Physic. Rev.*, 1932, 41, 337.

⁵ N. W. Taylor, *J.A.C.S.*, 1926, 48, 854.

lesser extent, depending on the number of ClO_2 molecules present, or there may be a small diamagnetic effect. From these considerations, it is obvious that it is possible to find the proportions of ClO_2 and Cl_2O_6 in the mixture if its susceptibility and those of the pure components are known.

Experimental.

Susceptibility Measurements.

The ClO_2 - Cl_2O_6 mixtures used in this research were prepared by mixing, at 0°C ., a stream of oxygen containing 75 per cent. by weight of chlorine dioxide, with a stream of ozonised oxygen containing about 10 per cent. ozone. The flow speeds were roughly in the ratio 1 : 8. Solid crystals of the hexoxide were deposited on the walls of the reaction chamber and after fractional distillation their melting-point was about $+3.5^\circ\text{C}$.

The mixture was finally distilled into the trap shown in Fig. 1a, which was cooled to -30°C . The hexoxide on warming and melting, ran down into the cylinder V. A vacuum was maintained to remove any traces of impurity formed by decomposition during this last operation. The cylinder, immersed in liquid air up to the level of the hexoxide, was then sealed off at the constriction and a glass hook sealed on the top. The specimen could then be stored indefinitely in a solid carbon dioxide-alcohol mixture.

A Guoy method was used for the magnetic measurements. The specimen was suspended from the arm B of a weighing balance (Fig. 1b), so that one end of the cylinder was in a uniform field of about 5500 Gauss and the other end in a position where the field was negligible.

The apparatus for cooling the specimen consisted of a copper tube up which passed dry nitrogen, in a Dewar vessel containing liquid air to cool the gas. This vessel was of a special design with a constriction at its centre in order that the gap between the pole pieces, P, P of the magnet should be as small as possible. The copper tube C was thermally insulated from the outside air by means of a glass tube G. This was continued into another copper tube D to allow the rising gas to be heated rapidly to room temperature to prevent condensation of water vapour on the suspension. Temperatures were measured by means of the copper constant thermocouple T, which was insulated from the copper tube by means of a glass tube and asbestos. This thermocouple was initially calibrated with a standard Pt—Pt.Ir couple suspended in the position to be occupied by the sample of the hexoxide mixture.

The force acting on the substance in a magnetic field is measured by "g" times the difference in weight ΔW with and without the field, and is given by the equation:—

$$F = \Delta W \cdot g = \frac{1}{2}(K_1 - K_2)AH^2,$$

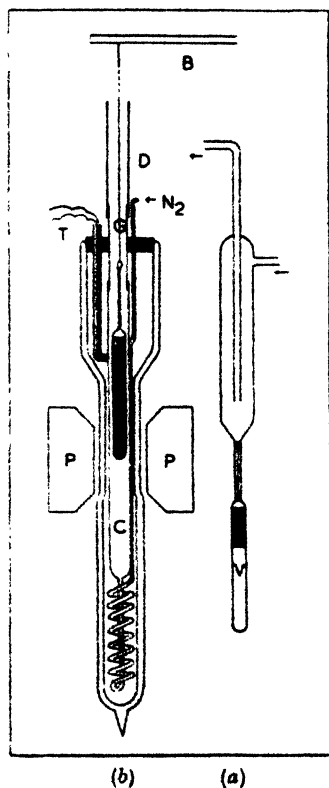


FIG. 1.—The apparatus.

where K_1 is the volume susceptibility of the specimen; K_2 that of the medium in which it is suspended (in this case nitrogen); H the magnetic field, and A the cross-section of the specimen. K_2 can be assumed as negligible in comparison with K_1 .

Values for ΔW were determined first for the cylindrical tube plus the hexoxide, for a series of temperatures. The values for the empty tube were then determined over the same temperature range. The whole apparatus was standardised by repeating with the tube filled with conductivity water to the level of the original hexoxide. From the value for water,* 0.72×10^{-6} , the volume susceptibility of the hexoxide can be calculated, using the relative values of ΔW . The mass susceptibility is obtained from this and the density at the freezing point.

Results.—The measurements were carried out over a temperature range $-40^\circ \text{C. to } +10^\circ \text{C.}$ This range was obtained by allowing the liquid air in the Dewar vessel to distil slowly away. Measurements above $+10^\circ \text{C.}$ could not be made, as the hexoxide decomposes, producing chlorine dioxide above this temperature. The results are shown in Fig. 2. Curve A is drawn through the values of ΔW for the tube filled with the

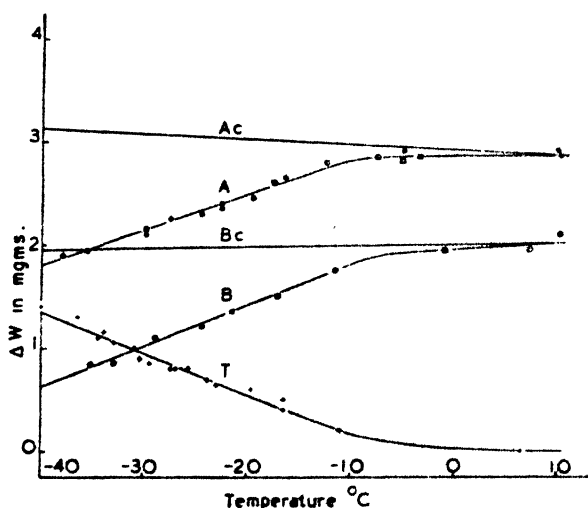


FIG. 2.—The results.

hexoxide mixture. Measurements were made on two successive days, those on the second being indicated by circles. The values of ΔW are negative (diamagnetic). The values for the empty tube are shown by curve T. In this case ΔW is positive. The values for the hexoxide mixture alone are shown by curve Ac, which is the sum of curves A and T. It is seen from the figure that the hexoxide mixture is diamagnetic throughout the temperature range and

that the susceptibility decreases with increasing temperature. The diamagnetism shows that Cl_2O_6 is in a $^1\Sigma$ state.

One series of measurements was made after leaving the specimen for fifteen minutes at 20°C. The results are shown by curves B and Bc. Owing to the strong paramagnetic effect of the dioxide (and oxygen) now present in the mixture—an effect which should decrease with rise in temperature—this curve lies well below that for the pure specimen, the amount of separation being approximately proportional to the absolute temperature.

Density Measurements.

From the weighings made for the above determinations the density was calculated fairly accurately and found to be 2.00 gms. per c.c. A more accurate determination was made by distilling about 1 c.c. of the hexoxide, used for the magnetic measurements, into a small graduated

* Landolt Börnstein, *Physikalisch-Chemische Tabellen*, 1923, p. 1203.

tube with a capillary neck. In this apparatus the coefficient of expansion was also found. The results were as follows:—

Density of the liquid hexoxide at $+3.5^{\circ}\text{C.}$. $2.023 \pm .003$ gms. per c.c.
 Specific volume 0.494 c.c. per gram.
 Coefficient of cubical expansion $12 \pm 3 \times 10^{-6}$ c.c. per c.c. per degree C.

Theoretical Susceptibilities of ClO_3 and Cl_2O_6 .

The molar susceptibility ($\chi_{\text{mol.}}$) of ClO_3 can be calculated from the simplified relation of Van Vleck⁷:—

$$\chi_{\text{mol.}} = \frac{4N\beta^2 S(S+1)}{3KT},$$

where N is the number of molecules per gram molecule; β the Bohr magneton, 0.9174×10^{-20} e.m.u.; S the spin quantum number, and K the Boltzmann constant. It is assumed that all the electrons, except the odd one, are paired, and therefore $S = \frac{1}{2}$. The mass susceptibility is then found by dividing $\chi_{\text{mol.}}$ by the molecular weight. The values so calculated for a number of temperatures are shown in column 2 of the Table.

Temperature.	Mass Susceptibilities $\times 10^6$ (Ergs gram ⁻¹ gauss ⁻²).			Per Cent. ClO_3 by Weight.	$K \times 10^3$.
	ClO_3 .	Cl_2O_6 .	Experimental.		
-40	19.15	-0.405	-0.264	0.721	2.54
-30	18.36	"	-0.250	0.775	2.94
-20	17.64	"	-0.255	0.826	3.34
-10	16.98	"	-0.251	0.886	3.85
0	16.36	"	-0.247	0.943	4.36
+10	15.79	"	-0.243	1.001	4.91

The value for the molar susceptibility of Cl_2O_6 can be calculated by adding Pascal's experimental atomic values.⁸ For Cl his figure is -20×10^{-6} e.m.u., and for oxygen -4.6×10^{-6} , thus giving a value for the molar susceptibility of -67.6×10^{-6} , and for the mass susceptibility of -0.405×10^{-6} . This figure is supported by that obtained from Pauling's theoretical ionic values.⁹ Here it is necessary to assume some such structure as $\text{Cl}^{7+} + \text{Cl}^{5+} + 6\text{O}^{2-}$ for Cl_2O_6 , which gives $\chi_{\text{mol.}} = -(1.2 + 5.7 + 6 \times 12.6) \times 10^{-6} = -82.5 \times 10^{-6}$. This is subject to a reduction of about 20 per cent., owing to the formation of linkages. The susceptibility thus becomes $\chi_{\text{mol.}} = -66.5 \times 10^{-6}$, which adds confirmation to the value taken for this work, $\chi = -0.405 \times 10^{-6}$. As diamagnetism is independent of temperature, it is unnecessary to make any correction for temperature variation.

⁷ J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities*, 1932, p. 274.

⁸ E. G. Stoner, *Magnetism and Matter*, 1934, p. 470; Müller-Pouillet, *Lehrbuch der Physik*, 1934, p. 717.

⁹ For the calculation of the theoretical ionic susceptibilities see Pauling, *P.R.S. A*, 1927, 114, 181; and for their application see Gray and Farquharson, *Phil. Mag.*, 1930, 10, 191, and Farquharson, *Phil. Mag.*, 1932, 14, 1003.

Discussion.

The value of the mass susceptibility of the chlorine hexoxide calculated from the values of ΔW in Fig. 2 are shown in column 4 of the Table. It is seen that the diamagnetism of the mixture is less than the theoretical value for Cl_2O_6 . This is probably due to the presence of a paramagnetic substance in equilibrium with Cl_2O_6 , and increasing in amount with rise in temperature. As the substance exists almost entirely as ClO_2 in the gaseous phase, it is most likely that there is some dissociation in the liquid and solid phases as well. The percentage by weight of the trioxide, calculated by assuming the difference between the experimental and theoretical values to be due exclusively to its presence, is given in column 5. Chlorine dioxide, if present, would act exactly as the trioxide as regards its effect on the susceptibility, and the values in this column would have to be reduced by a fixed amount. From the melting-point and the colour of the specimen at low temperatures, properties which are markedly affected by small amounts of chlorine dioxide, it is considered that the effect of traces of this oxide is not greater than the following limits of error :—

These observations are subject to a number of possible errors. The weighings were carried out to 1/20th mgm. Assuming that the theoretical values of the mass susceptibilities are correct, the errors in weighing lead to an uncertainty in the values in column 5 of ± 0.05 . The theoretical values for ClO_2 are probably sufficiently accurate not to affect these limits of error. The additivity principle used to determine the value of -0.405×10^{-6} for Cl_2O_6 has been fairly well established,⁸ but its application is subject to confirmation by a study of other diamagnetic oxides of chlorine. Any error here would lead to a disproportionate error in the final results. The error in absolute temperature is rather indefinite, due both to the time lag in the warming of the specimen and the temperature gradient up the cylinder. The total time of the experiment was two and a half hours and near the melting-point this error was not more than a few degrees.

The values of the equilibrium constant K_c are given in the last column. The concentrations are expressed in gram molecules per litre. The logarithm of this constant, when plotted against the reciprocal of the absolute temperature, gives a straight line and the results may be expressed by the following equation :—

$$\log_{10} K_c = C - \Delta U/2.3 RT = -0.974 - 1730/2.3 RT.$$

The heat of dissociation of Cl_2O_6 is therefore 1730 ± 500 calories per gram molecule. No break in the curve was observed at the melting-point.

The low dissociation in the condensed state and the almost complete dissociation in the gaseous state⁸ are not incompatible. Should an equilibrium constant of the same order as that above apply to the gaseous state, the equilibrium would be almost entirely on the side of the ClO_2 , owing to the very low vapour pressure.

The above work was carried out with the financial assistance of the Department of Scientific and Industrial Research and of Imperial Chemical Industries, Ltd.

Summary.

The susceptibility of chlorine hexoxide has been measured over a temperature range -40° to $+10^{\circ}$ C. The density and coefficient of cubical expansion have also been determined.

On the basis of theoretical values for the susceptibilities of Cl_2O_6 and ClO_2 , the percentage of ClO_2 present in the mixture at various temperatures has been calculated, together with the corresponding equilibrium constants.

An approximate value for the heat of dissociation has been determined from these constants.

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TRANSPORT NUMBERS OF PARAFFIN-CHAIN* SALTS IN AQUEOUS SOLUTION.

PART I.—MEASUREMENT OF TRANSPORT NUMBERS OF
CETYLPIRIDINIUM AND CETYLTRIMETHYLAMMONIUM
BROMIDES AND THEIR INTERPRETATION IN TERMS
OF MICELLE FORMATION. WITH SOME DATA ALSO FOR
CETANE SULPHONIC ACID.

By G. S. HARTLEY, B. COLLIE,† AND C. S. SAMIS.‡

Received 13th January, 1936.

The difficulty of drawing correct conclusions about micelle formation from conductivity data alone has been discussed in some detail elsewhere.¹ By micelle formation we mean the aggregation of large organic ions of like sign which occurs in aqueous solutions of several types of organic salts of high equivalent weight. Although aggregation of ions of like sign only will, according to the well-known reasoning of McBain,² increase their mobility, micelle formation may not produce an increase of equivalent conductivity. If the micelles are large, the aggregation will considerably increase the effect of coulomb attraction between the constituent ions and ions of opposite sign (which we shall call "gegenions"). The consequent adherence of gegenions to the micelle will tend to reduce both the mobility of the micelle and the equivalent conductivity. The effect on the latter will be relatively greater than on the former. The direct braking effect of the Debye-Hückel "atmospheres" will also reduce both these quantities, and probably the former relatively more than the latter, but, although in micelle-containing solutions their effect will be great, it will probably be less important than that of the gegenions actually adhering to the micelle.³ If, therefore, micelle

* A more exact name which will be used in subsequent publications in place of the "long-chain" salts used in earlier ones.

† Experimental work entirely done by the latter authors.

‡ Moilliet, Collie, Robinson and Hartley, *Trans. Faraday Soc.*, 1935, **31**, 120.

¹ McBain, *ibid.*, 1913, **9**, 99.

² Hartley, *ibid.*, 1935, **31**, 31.

formation causes a decrease rather than an increase of equivalent conductivity, we may still find an increased mobility for the organic radical, and shall almost certainly find an increase of its transport number.

This is well illustrated by the equivalent conductivity-concentration curves for the two dyes, methylene blue and "meta" benzopurpurine, and for the paraffin-chain salt, cetylpyridinium chloride.¹ The first has an equivalent conductivity rising *above its infinite dilution value* in very dilute solution, a phenomenon which seems to admit no other interpretation than the formation of (probably small) micelles. The second, which transport number measurements have conclusively shown to contain micelles, has an *apparently* normal conductivity. The third shows, at a concentration of about $N/1000$, a very sudden *fall* of equivalent conductivity which, there is nevertheless very strong evidence^{4, 6} to show, is accompanied by the formation of large micelles.

In the present work, transport number measurements on two paraffin-chain salts are described. The objects in carrying out this work were three: (a) to obtain yet more evidence than was before available that the sudden fall of conductivity is due to the formation of micelles and consequent association of the gegenions with them; (b) to measure the mobility of the micelles and, if possible, to obtain some idea of the fraction of the gegenions adhering to them and, hence, of the number of paraffin-chain ions contained in each; (c) to find a satisfactory explanation of the *rise of equivalent conductivity* with increasing concentration which is found in most paraffin-chain salts in moderately concentrated solutions, since our knowledge that micelle formation produces the steep *fall of equivalent conductivity* found in the dilute solutions necessitates a reconsideration of McBain's almost classical theory of the former phenomenon.

Experimental.

The method and apparatus used for the transport number determinations have been fully described elsewhere.⁴ A brief outline only will be given here. When practicable, the moving boundary method is greatly to be preferred to the Hittorf method, since it enables continuous measurements to be made instead of depending on four analyses only (and frequently two are not practicable, owing to the non-existence of sufficiently accurate analytical methods). In each experiment with the moving boundary method we have an internal check on the accuracy of the results, and moreover the whole experiment can be carried out in a shorter time than with the Hittorf method. If we wish to determine the transport numbers of large radicals directly by the moving boundary method, however, we shall frequently be faced with difficulty in finding salts to act as indicators, because these must have a radical of like polarity which has a *lower* mobility than the one we are concerned with. For the largest and slowest organic radicals it becomes necessary, therefore, for the radical which is to be investigated to *follow* one which is *faster*. Measurement of the current and volume velocity of the boundary gives us the transport number of the *leading* radical, because the concentration of this remains constant at its initial value in the solution into which the boundary is advancing. It does not, however, give us the transport number of the *following* radical, because the concentration of the latter, in the solution which the boundary leaves behind, is determined, not by its initial concentration (except insofar as convection may cause disturbance), but by the concentration of

¹ Malsch and Hartley, *Z. physik. Chem.*, 1934, 170A, 321.

² Murray and Hartley, *Trans. Faraday Soc.*, 1935, 31, 183.

³ Hartley, Drew and Collie, *ibid.*, 1934, 30, 648.

measurements here recorded have been obtained with the new apparatus, which gives very much more concordant results, and these agree very well with the mean results obtained in the old apparatus. This new apparatus will be described in detail in a later publication.

The salts cetylpyridinium bromide and cetyltrimethylammonium bromide were used in this investigation. Potassium, or, in some cases, barium bromide, was used as leading electrolyte. Platinum gauze immersed in ferric bromide solution provided a satisfactory non-gassing cathode which did not give rise to anions more mobile than bromide. Silver-plated platinum gauze served satisfactorily for the anode, solid silver bromide being quantitatively formed. Owing, presumably, to interference of the paraffin-chain salt with the crystal growth, the silver bromide did not adhere to the electrode, but formed instead a fine precipitate.

Both paraffin-chain compounds were obtained from cetyl bromide kindly supplied by Imperial Chemical Industries, Ltd., and subjected to careful fractionation by our colleague, Dr. N. K. Adam, to whom we are greatly indebted. Its bromine content was found to be 26.25 ± 0.5 , agreeing well with the theoretical 26.2 (C_{14} has 28.8 and C_{16} , 24.9 per cent.). Cetylpyridinium bromide was prepared by heating the cetyl bromide with 20 mols. per cent. excess of pyridine, purified by the method of Arndt and Nachtwey,⁷ with constant stirring at 120–30° C., for four hours. The product was several times recrystallised from water and then from redistilled acetone, and dried in a vacuum desiccator over phosphorus pentoxide. The bromine content, found gravimetrically by precipitation with $AgNO_3$ in alcoholic solution, was 20.68 per cent. (theoretical 20.79 per cent.). The trimethylammonium salt was prepared by refluxing cetyl bromide with excess of 10 per cent. solution of trimethylamine in nitromethane (prepared by boiling off trimethylamine from 30 per cent. aqueous solution, through lime, into nitromethane), using an ice-cooled condenser to prevent loss of trimethylamine. The product was washed with acetone, recrystallised several times from water, and dried over phosphorus pentoxide. Bromine content 21.79 per cent. (theoretical 21.93 per cent.). Both preparations gave perfectly clear aqueous solutions above about 30° C. The water used had a specific conductivity $0.2-0.4 \times 10^{-6}$ ohms⁻¹ cm.⁻¹ as collected in CO_2 -free air from a special still, but no precautions were taken to prevent access of CO_2 in the transport number apparatus.

All solutions were made up by volume * at 35° C., at which temperature all the measurements here recorded were made. Densities were separately determined in order to convert the concentrations to the mass-of-solvent basis for calculation of the Hittor' transport numbers.⁸ Knowledge of the densities was also necessary to confirm that the Kohlrausch solution in the transport apparatus was less dense than the leading solution below it, a condition which is, of course, necessary for stability of the (descending) boundary.

Conductivities were determined by means of a direct-reading alternating current bridge, employing three frequencies: about 1000, $1000 \times \sqrt{2}$ and 1000×2 cycles per sec. The apparent leak in the leads from cell to bridge (due to non-ideal capacity) and errors due to the oscillator-bridge coupling (arising because the connection of cell to the dial resistance box was directly

⁷ Arndt and Nachtwey, *Ber.*, 1926, **59**, 448.

* In the manipulation of these cationic paraffin-chain salt solutions in glass vessels, difficulty is frequently encountered owing to their leaving the glass in a peculiar condition, so that when water is introduced into a vessel that has contained a solution, the walls behave as though they were extremely greasy. Probably the cations are adsorbed "head-on" to the negatively charged glass, and thus leave exposed a monomolecular layer of paraffin "tails." The solutions themselves will wet this layer unless they are extremely dilute. Small air bubbles also adhere to glass or platinum very tenaciously when a very dilute solution is used. The layer may be removed by washing with alcohol or acetone.

earthed) were determined by calibration with a standard resistance box in the cell position. Error due to resistance-capacity shunts in the cell when high resistances were being measured was eliminated by extrapolation against square of frequency to zero frequency. The cells used in this work were of the type described by Robinson and Moillet,⁸ except that, for the most dilute solutions, a large cell was used of a type that permitted dilution to be carried out in the cell without access of carbon dioxide. The electrodes were blackened except in the dilution cell, which was used only for very low concentrations. Equivalent conductivities are given in Table I.

TABLE I.—TOTAL EQUIVALENT CONDUCTIVITIES.

Cetylpyridinium Bromide		Cetyltrimethylammonium Bromide.	
gm. equiv. litre at 35° C.	cm. ² ohm. (gm. equiv.).	gm. equiv. litre at 35° C.	cm. ² ohm. (gm. equiv.).
0.00040	118.9	0.00038	120.2
0.00055	118.2	0.00062	119.2
0.00075	116.2	0.00080	118.7
0.00087	107.1	0.00105	113.1
0.00099	99.0	0.00157	88.3 ₆
0.00121	86.9 ₆	0.00236	67.8 ₀
0.00156	74.9 ₆	0.00477	50.6 ₄
0.00247	60.3 ₇	0.00498	49.7 ₆
0.00345	52.8 ₂	0.00868	40.5 ₁
0.00499	46.5 ₄	0.0114 ₂	37.7 ₂
0.00740	41.5 ₂	0.0247 ₃	32.0 ₁
0.0138 ₆	35.8 ₉	0.0534 ₈	29.5 ₇
0.0355 ₁	31.0 ₂	0.0648	29.2 ₄
0.1090 ₆	20.1 ₄	0.0692	29.0 ₆
		0.173 ₆	28.3 ₂
		0.278 ₆	27.0 ₆
		0.409 ₇	27.3 ₁
		0.421 ₄	27.7 ₄

The data for the transport number determinations are collected in Table II. From the known volume concentration of KBr or BaBr₂ (column 1), and the volume concentration (column 7) of paraffin-chain salt in the Kohlrausch solution, determined by conductivity the transport number of the organic radical (column 8) was calculated from the Kohlrausch equation (1), the concentrations being converted to the mass-of-solvent basis for use in this equation. In column 2 is given the mean of the numerical deviations of the resistance of the Kohlrausch solution from the mean resistance, expressed as a percentage of the latter, and in column 3 the time over which readings included in the average were taken (at half-hour intervals). In the column headed "drift" is given the average resistance for the first half of this time subtracted from that for the latter half, expressed as percentage of the complete average. The time that was allowed to elapse before readings were included in the average is given in column 5, and the initial concentration of the paraffin-chain salt solution in column 6. It will be noticed that results obtained with the new apparatus (denoted by *), and those obtained using BaBr₂ in the leading position (†) are in good agreement with the other results. BaBr₂ was used to check the figures obtained with KBr because, owing to the great density difference of the leading and Kohlrausch solutions when the former is used, error due to convection, which is the most probable source of error in the more concentrated solutions, will be greatly reduced. The

⁸ Robinson and Moillet, *Proc. Roy. Soc.*, 1934, 143A, 360.

TABLE II.—TRANSPORT NUMBER DATA.

Gm. Equiv. Litre KBr or BaBr ₂ .	Kohlrausch Resistance.				Gm. Equiv./Litre. Paraffin-chain Salt.		Transport Number.
	Dev. Per Cent.	Hours Const.	Drift Per Cent.	Hours before Const.	Initial.	Kohl- rausch.	
Cetylpyridinium Bromide.							
0.00143	1.5	8.5	— 1.9	1.0	0.0007	0.00065	0.22 ₁
0.00172	0.8	12.0	+ 0.7	3.0	0.0007	0.00078	0.21 ₉
0.00171	0.4	7.0	— 0.5	0.5	0.0032	0.00476	1.34
0.00216	0.3	4.5	+ 0.5	5.5	0.0032	0.00668	1.49
0.00303	0.3	5.5	— 0.7	3.5	0.0032	0.00998	1.59 ₃
0.00434	0.5	5.0	+ 0.3	3.5	0.0133	0.0148 ₉	1.66 ₁
0.00435	0.7	3.5	— 0.9	5.5	0.0178	0.0148 ₁	1.65 ₄
0.01022	0.5	6.5	— 1.3	2.0	0.0312	0.0339	1.62 ₃
0.01019	1.0	6.0	— 1.9	2.5	0.019	0.0339	1.62 ₃
0.0451*	0.1	4.0	— 0.2	6.0	0.0525	0.116 ₃	1.29 ₃
0.0401*†	0.0	6.0	— 0.0	3.0	0.0871	0.118 ₉	1.30 ₆

Cetyltrimethylammonium Bromide.

0.00175	0.2	6.0	+ 0.7	12.0	0.0017	0.00132	0.38
0.00200	0.4	3.0	+ 0.5	10.0	0.0017	0.00182	0.43
0.00168	0.6	4.0	0.0	0.0	0.0141	0.00507	1.4 ₆
0.00434	0.1	3.0	0.0	5.0	0.0138	0.0146 ₃	1.63 ₃
0.00661*‡	0.0	6.0	0.0	4.0	0.037	0.0242 ₇	1.62 ₆
0.0112	0.2	8.0	+ 0.5	4.0	0.0229	0.0300	1.55 ₃
0.0184	0.2	6.0	— 0.1	6.0	0.042	0.0056 ₆	1.48 ₃
0.0292	0.1	5.0	0.0	4.0	0.0780	0.0832	1.41 ₅
0.0500	0.1	3.0	0.0	6.0	0.0446	0.128 ₈	1.34 ₆
0.0757*	0.0	4.0	0.0	5.5	0.1872	0.184 ₁	1.25 ₆

* Distinguishes results obtained with the new apparatus.

† BaBr₂ used as leading electrolyte. T_{Ba} taken = 0.425.‡ BaBr₂ used as leading electrolyte. T_{Ba} taken = 0.436.

Volume velocity of the boundary, if not balanced, about 0.55 c.c./hr. in old apparatus and 0.67 c.c./hr. in new, these being about 10 per cent. in excess of the piston velocities.

good agreement is evidence that convection is not causing appreciable error.

The value of T_K in the KBr solutions was taken to be 0.483 at all the concentrations used, in accordance with the measurements of Longworth⁹ at 25° C., assuming the temperature effect on transport number to be negligible for this salt, as would be expected from the temperature coefficients of ionic conductivities given by Kohlrausch and Holborn.¹⁰ For T_{Ba} in BaBr₂, the values for BaCl₂ at 25° C., at the relevant concentrations, were taken from the work of Jones and Dole¹¹ and allowance made for the bromide-chloride difference and for the temperature change on the basis of the figures given by Kohlrausch and Holborn. This gave T_{Ba} in BaBr₂ at 35° C., 0.7 per cent. less than T_{Ba} in BaCl₂ at 25° C. The figures obtained in this way are probably more accurate than any direct measurements at present published. As the transport number of the paraffin radical in our results is simply proportional to the T_K or T_{Ba} value (the concentrations being unaffected) correction may be made at once when more accurate data are available.

⁹ Longworth, *J. Amer. Chem. Soc.*, 1935, **57**, 1185.

¹⁰ Kohlrausch and Holborn, *Das Leitvermögen der Elektrolyte* (Leipzig, 1916).

¹¹ Jones and Dole, *J. Amer. Chem. Soc.*, 1929, **51**, 1073.

Within a certain range, the transport number in the paraffin-chain salt solution is changing so rapidly with concentration that two different Kohlrausch solutions could be obtained with the use of the same leading solution.* The lower one was obtained by starting with a still lower paraffin-chain salt concentration, and the higher by starting with a still higher concentration. The adverse density gradient that must have existed in experiments where the latter procedure was adopted did not give rise to convection trouble, presumably because the low concentrations and the lightness of these salts in water did not cause a density different sufficient to compete with the upward bulk flow of the solution. It was not thought necessary to attempt to obtain any points in the middle of this range, which is about from $N/700$ to $N/300$.

Discussion of Results.

I. Qualitative.

The total equivalent conductivities and the transport numbers of the organic radicals in the two paraffin-chain salts are plotted against the square root of volume concentration in Fig. 2. The former quantity falls very steeply and rather suddenly at about $N/1000$, as in other unhydrolysed salts with 16 carbon atoms in the chain.^{12, 5} The transport numbers rise very rapidly in the range where the total equivalent conductivities fall, and reach values much above unity in concentrations well below $N/100$. The greater-than-unity values mean, of course, that the bromide transport numbers are negative, *i.e.* that more bromine is being carried towards the cathode by more-than-univalent cations than is migrating in the free state to the anode. In a salt whose single cations are univalent, this admits of no other explanation than the formation of multiple cations—micelles.

Below $0.0008N$ we have experimental points which, though they are not very accurate, are obviously not far removed from the value -0.22

* Reference to Fig. 1 which is a qualitative diagram in which the variation is exaggerated for the sake of clarity, will show that there must, in general, be three solutions to the Kohlrausch equation if there is more than one. For a given leading solution the

three Kohlrausch concentrations will be represented by the intersections with the transport number curve of a straight line whose slope is equal to T_R/C_R . In the central region it is clear that dT/dC is greater than T/C and, therefore, concentration disturbances will tend to be propagated more rapidly than the boundary itself, a possibility discussed by Hartley and Moilliet.¹³ It can be shown that the intermediate Kohlrausch concentration is not experimentally attainable,

and that, if an initial concentration of paraffin-chain salt near to it were used, a Kohlrausch solution of either the one extreme or the other would be obtained, but only as a small region moving after the boundary and gradually increasing in depth.

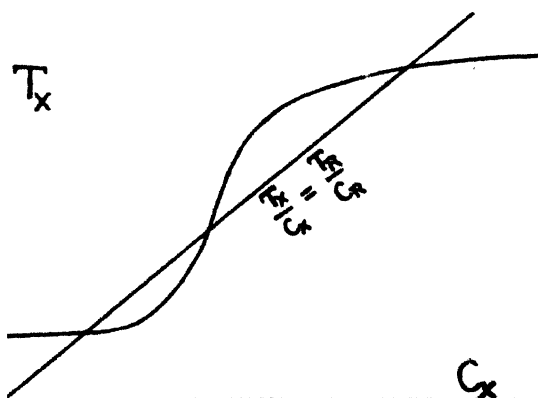


FIG. 1.

¹² Lottermoser and Püschel, *Koll. Z.*, 1933, 53, 175.

¹³ Hartley and Moilliet, *Proc. Roy. Soc.*, 1933, 140A, 141.

—predicted for infinite dilution from the conductivity data: below this concentration there is presumably no appreciable aggregation. The abruptness of the change is easily explicable by the mass-action law according to the reasoning of Bury,^{14, 5, 15} if the micelles formed are large and if small aggregates are not present in considerable amounts.

With regard to both conductivity and transport numbers, the two salts studied are extremely similar, the chief differences being that the critical concentration for the pyridinium compound is slightly lower than that for the trimethyl-ammonium compound (0.00075 as against 0.0009*N*), and that the maximum transport number is slightly higher. For the sake of simplicity, therefore, we shall confine the further discussion to the latter salt, for which the data are rather more extensive.

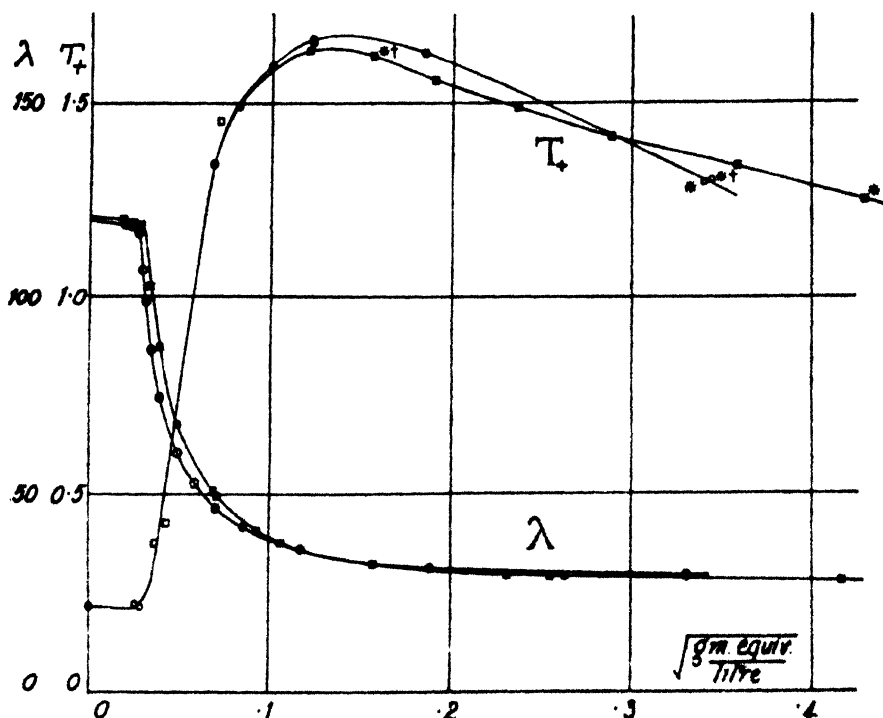


FIG. 2.—Total equivalent conductivity and paraffin-chain transport number for cetylpyridinium (O) and cetyltrimethylammonium (□) bromides at 35° C. * and † distinguish points obtained with new apparatus and BaCl_2 , respectively.

In Fig. 3 is plotted the equivalent conductivity (μ) of the organic radical.* This rises very steeply in the critical region from the low value characteristic of large simple organic ions to a maximum of about

¹⁴ Jones and Bury, *Phil. Mag.*, 1927, 4, 841; Grindley and Bury, *J. Chem. Soc.*, 1929, 679; Davies and Bury, *J. Chem. Soc.*, 1930, 2263.

¹⁵ Hartley, "Aqueous Solutions of Paraffin-chain Salts," *Actualités Scientifiques*, Hermann, Paris. In press.

* We use the expression "equivalent conductivity" rather than "mobility" for this quantity expressed in the ordinary units ($\text{ohm}^{-1} \text{cm}^2 (\text{gm. equivalent})^{-1}$), because it has not the dimensions of a velocity per unit potential gradient or unit force. We use "radical" to signify that the property is measured for all ions of a particular kind in no matter what state of combination they occur. See Hartley and Moilliet.¹⁵

69 at a concentration of about $N/200$. The rise of the equivalent conductivity of this radical *above its infinite dilution value* is the most direct evidence possible¹ of aggregation. The *fall* of *total* equivalent conductivity during this range of concentration is due to the enormous reduction in conductivity of the bromide ions consequent on their attachment to the micelles.

This conclusion necessitates some modification of McBain's original theory of the constitution of soap solutions, which has been extended by Norris,¹⁶ and McBain and Williams¹⁷ to cetane sulphonic acid. The latter substance shows the critical fall of equivalent conductivity at about the same concentration as the two compounds at present under consideration.* The mass action law makes it extremely probable that,

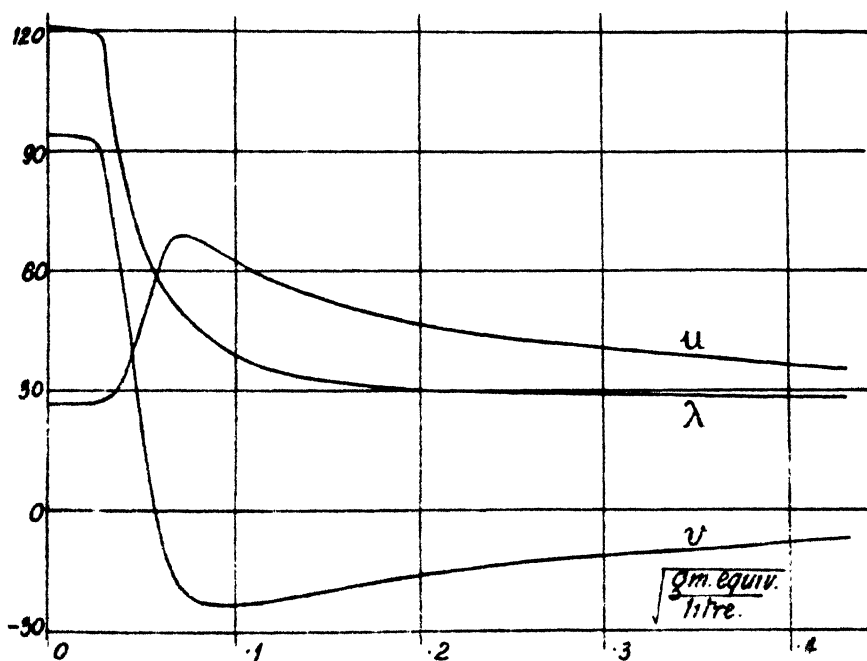


FIG. 3.—Equivalent conductivities of the component radicals and the whole salt, cetyl-methylammonium bromide, 35° C.

from this concentration upwards, almost all additional paraffin-chain ions go to form micelles, and indeed it is probable that the concentration of free paraffin-chain ions decreases *absolutely*.¹⁸ At a concentration of $N/100$ it is, therefore, almost certain that there will only be a very small fraction of cetane sulphonate ions in non-aggregated forms. In McBain's composition diagram,¹⁹ however, we find that the micelle is only supposed to comprise some 15 per cent. of the total even at a concentration of

¹⁶ Norris, *J. Chem. Soc.*, 1922, 121, 2161.

¹⁷ McBain and Williams, *J. Amer. Chem. Soc.*, 1933, 55, 2250.

* Unpublished measurements by C. S. H.

¹⁸ Murray, *Trans. Faraday Soc.*, 1935, 31, 206.

¹⁹ See *International Critical Tables*, 1929, 3, 448.

$N/10$. Micelles come into being at far lower concentrations than was thought by McBain to be the case.*

The necessity for this modification was appreciated by Lottermoser and Püschel in their work on higher alkyl sulphates,⁹ but these authors postulated the formation of "neutral colloid" at the critical concentration. This enabled them to postulate the formation of "ionic micelle" in higher concentrations to account for the rise of the equivalent conductivity in these concentrations (ca. $N/20 - N/2$), a phenomenon which occurs in these compounds as well as in the well-known case of the soaps.²⁰ We find, however, that the first aggregates formed are by no means neutral, and that the total equivalent conductivity falls despite an *increased* mobility of the organic radical. This throws considerable doubt on the explanation of the rising conductivity, put forward by McBain and accepted by Lottermoser, as a direct effect of the replacement of a less by a more mobile form of the organic ions. It is probable that the micelles which cause a rising equivalent conductivity in methylene blue¹ are small. Those which, despite their high mobility, cause the steep fall of equivalent conductivity in paraffin-chain salts are probably much larger. It seems unlikely that still larger micelles (and any formed in higher concentrations must presumably be larger) would reverse the effect.

In the two salts here described, a rise of equivalent conductivity, comparable with that found in the salts with paraffin-chain anions, does not occur. The equivalent conductivity of the trimethylammonium compound (which has been investigated at higher concentrations than the pyridinium compound) does, indeed, rise slightly, above $\cdot 3N$, but from $\cdot 05N$ to $\cdot 2N$, where the equivalent conductivity of cetane sulphonic acid rises by about 20 per cent., that of the two bromides is still falling, though very slightly. The equivalent conductivity of the *bromide radical does*, however, *rise* in this range. This gives us an important clue to what is really happening in the other salts. The almost constant equivalent conductivity in the two bromides is almost as remarkable as the rise in the case of salts of paraffin-chain anions. Analogy with ordinary electrolytes would lead us to expect a steady and fairly rapid fall. Clearly, forces are in all cases operating against those normally considered, and it seems most probable that the difference is one of degree, these forces being powerful enough to reverse the normal effect in some cases, and, in others, only to counterbalance it. Do these forces, therefore, affect the total equivalent conductivity through the contribution to it of the Gegenions? To decide this question, we must see what variation with concentration is found for the equivalent conductivities

* Recently²¹ McBain has concluded "most of the transition between simple crystalloid and colloidal electrolytes takes place between $0\cdot 05$ and $0\cdot 15N$ for undecyl and 'lauryl' (C_{12}) sulphonic acids and in still more dilute solutions in 'myristyl' (C_{14}) sulphonic acid." One would expect, on any theory, that further increase of chain length would lower the transition concentration still more, but McBain does not say whether his conclusions with regard to the C_{12} compound are now modified, except that "in previous diagrams boundaries should be raised by a few per cent." (italics mine—G. S. H.), nor does he make any mention of the "critical concentration" phenomena. In the earlier papers of McBain and collaborators the steep fall of equivalent conductivity in the dilute solution was attributed to extensive formation of "simple undissociated" soap (or sulphonic acid) which is a highly improbable occurrence.¹⁸ It is not clear from the last paper how far this interpretation is now modified.

²¹ *J. Amer. Chem. Soc.*, 1935, **57**, 1920.

²⁰ See, i.e., Bunbury and Martin, *J. Chem. Soc.*, 1914, 105, 417.

of the component radicals, in the case of salts which do show a rise of total equivalent conductivity.

The transport data of McBain and Bowden²¹ for potassium oleate and laurate, of Holroyd and Rhodes²² for the former salt (distinguished by *) and of Laing²³ for sodium oleate, are combined in Table III. with

TABLE III.

Salt.	Concentration.	λ .	T.	v .	u .
Potassium Oleate 18° C.	0.25 Nw	34.0	{ 0.75	{ 25.5	8.5
	0.25 N*		{ 0.72	{ 24	10
	0.50 Nw	37.0	0.70	25.9	11.1
Potassium Laurate 18° C.	0.2 Nw	41.8	0.67	28.0	13.8
	1.0 Nw	47.1	0.55	25.9	21.2
Sodium Oleate 18° C.	0.2 Nw	19.8	1.22	24.2	-4.4
	0.4 Nw	20.8	1.12	23.3	-2.5
	0.5 Nw	21.2	1.09	23.1	-1.9
	0.6 Nw	21.7	1.05	22.8	-1.1
Cetane Sulphonic Acid 50° C.	0.013 Nv	146	0.58	85	61
	0.046 Nv	135	0.52	70	65
	0.073 Nv	143	0.46	66	77
	0.162 Nv	159	0.30	48	111

the conductivity figures given by McBain, Laing and Titley.²⁴ Here v denotes the equivalent conductivity of the fatty radical, and u that of the Gegenions as a whole. It will be seen that, for all these soaps, it is u which rises as λ rises, while v , except in the case of potassium oleate, falls. The lowest concentration of this salt, however, for which transport data are available, is already above the range in which most of the rise of λ occurs. In this table are given also data obtained by one of us (C. S. S., will be published in detail later) by the balanced boundary method, for cetane sulphonic acid in the range of concentrations where the very marked rise of λ occurs. Here there is no doubt that v falls quite rapidly while λ rises, and it is the great increase in the equivalent conductivity of the gegenions which causes the rise of λ .

It was mentioned above that McBain, and Lottermoser following him, explained the rise of total equivalent conductivity as a *direct* effect of replacement of a less by a more mobile form of the fatty ions. We see from the figures that this cannot be a generally valid explanation. The mean mobility of all the fatty ions is *not* generally increasing as the total equivalent conductivity rises. Lottermoser's explanation might, however, be *indirectly* valid. In assuming that, with increase of moderately high concentration, "neutral colloid" is replaced by "ionic micelle," he assumes that the total extent of dissociation of gegenions from micelles increases. As his "neutral colloid" cannot be quite uncharged and if his "ionic micelle" is only a little more highly charged, or present in only small amount, the increasing depression of the micelle mobilities by Debye-Hückel atmospheres might outweigh the effect of increasing charge and cause a net fall of mobility of the fatty radical. The effect

²¹ McBain and Bowden, *J. Chem. Soc.*, 1923, 123, 2417.

²² Holroyd and Rhodes, *ibid.*, 1919, 115, 1279.

²³ Laing, *J. Physik. Chem.*, 1924, 28, 673.

²⁴ McBain, Laing and Titley, *J. Chem. Soc.*, 1924, 125, 438.

of liberation of the gegenions, increasing the conductivity contribution of those set free from a considerably negative to a positive value, might very well outweigh any depression of the mobility of those already free, and produce the observed rise of the resultant mobility of the gegenions as a whole, and even, through this quantity, of the total equivalent conductivity.

If we consult McBain's constitution diagrams¹⁹ for soaps, we see that this increase in the fraction of free gegenions (given by the combined width of the "simple fatty ion" and "ionic micelle" fields) is also implicit in his calculations. Recently, McBain and Betz²⁰ have made this same assumption explicitly and obtained valuable new evidence of its validity. They find that the osmotic coefficient (from freezing-point determinations) and "hydrogen ion activity coefficient" (from E.M.F. of cells with liquid junctions) in solutions of sulphonic acids, also increase with increase of moderately high concentrations. Lottermoser and Püschel⁹ found a similar increase in the "silver ion activity coefficient" in solutions of silver alkyl sulphates. While the evidence from neither source is conclusive, since the Debye-Hückel contribution to the osmotic coefficient may increase without there being any change in the real degree of dissociation, and since the interpretation of cells with liquid junctions is a very difficult and uncertain procedure, particularly where very unsymmetrical electrolytes are involved, these conclusions certainly make the assumption of an increase in the fraction of free gegenions much more probable. Further suggestive evidence in the same direction is found in the peculiar variation of the alkalinity of pure soap solutions with concentration. McBain and Martin²¹ found that the alkalinity of the concentrated solutions decreased *absolutely* with increase of concentration. This means that the fraction of acid in the undissociated form (which is presumably all contained in aggregates) decreases with increase of concentration of a solution in which the hydrogen ion concentration is *increasing*.^{*} The micelles can, therefore, lose hydrogen ions despite the increase in the bulk concentration of the latter, and it is, therefore, probable that other cations can also be liberated under similar apparently unsuitable conditions.

It seems difficult to account for the fact that the rise of total equivalent conductivity is caused by a rise of that of the gegenions, as a whole, and not by a rise of that of the fatty radical, in any other way than by liberation of gegenions from the micelles. We must not, however, lose sight of the fact that, in a solution where the mobility of the gegenions is low because many of them are carried backwards by micelles, a fall in the mobility of the micelles will produce, in the absence of any other changes, a rise in that of the gegenions. In a solution where micelles of diverse sizes are present, it does not seem obvious what the effect on the total equivalent conductivity may be. In a more detailed discussion in the third section, we come, however, to the conclusion that the conductivity and transport data for cetane sulphonic acid do almost certainly necessitate the assumption that gegenions are re-liberated, whether one or two fundamental types of micelle, each comprising a range of minor

¹⁹ McBain and Betz, *J. Amer. Chem. Soc.*, 1935, **57**, 1909, 1913.

²⁰ McBain and Martin, *J. Chem. Soc.*, 1914, 105, 957.

^{*} This is the important difference from the case of the hydrolysis of the salt of a simple weak acid. In the latter the fraction of acid in the undissociated form also decreases with increase of concentration, but so does the concentration of hydrogen ions.

variations, is assumed. This being so, it seems to us unnecessary to assume, as Lottermoser does, the existence of two different types.* May not the re-liberation of gegenions be just as likely an effect of concentration on micelles of essentially the same type? We are not wholly without a plausible physical picture of such a concentration effect. The fraction of the gegenions which adhere to the micelle will be governed mainly by their concentration in the free state near its surface. This will be greater than their concentration in bulk, and the factor by which the latter must be multiplied to give the former, which may be obtained approximately by graphical integration of the Boltzmann-Poisson equation, decreases with increase of concentration.³ For large micelles this decrease is so great as to make the concentration of gegenions near the surface of the micelle *tend* towards a *constant* value. It is not, therefore, difficult to understand that the fraction of free gegenions will *not decrease* very rapidly. These conclusions are based on the picture of a spherically symmetrical atmosphere around the micelle. For two reasons this picture is seriously incomplete. First, the charges on the micelle are at discrete points, fairly far apart, and the near portions of the atmosphere will, therefore, collect, as it were, into nodules. Secondly, the occasional near-approaches of micelles to one another will produce temporary distortions which cannot be averaged out in any simple way. It is only necessary for these distortions to have more effect in reducing the atmosphere concentration at some times and places than in increasing it at others to give us a mechanism for the decrease of the number of gegenions attached to each micelle.

II. General Relationships Between Conductivities in a Solution Containing Micelles, not all of one Kind.

Before making a closer examination of the rising equivalent conductivity or attempting to form some estimate of the size of the micelles formed in dilute solutions, it will be necessary to derive certain fundamental equations relating the various equivalent conductivities.

The nomenclature and definitions of Hartley and Moilliet¹² will be used, but we shall replace the symbol f of Hartley and Robinson²⁷ by θ , in order that in later papers the former symbol may be used without confusion for the activity coefficient, in accordance with general usage.

Let a fraction x_p of all the paraffin-chain ions in solution exist in the form of micelles of type P, each containing m_p paraffin-chain ions with n_p gegenions adhering to them. Let the mobility of the micelle (its mean velocity in cms./sec. in a field of 1 volt/cm.) be L_p . The contribution made by the paraffin-chain ions in the form of this micelle to the total specific conductivity will be $cx_p L_p F$ where C is the total equivalent concentration (equivalents per c.c.) and F is the Faraday number in coulombs. Replacing the product $L_p F$ by l_p , the latter being the *equivalent conductivity* of paraffin-chain ions in micelles of type P, and dividing by c , we get, for the contribution which the paraffin-chain ions in these micelles make to the total equivalent conductivity, $x_p l_p$. If we assume the whole of the paraffin-chain ions to be included in this treatment (i.e., confine ourselves, as we shall do, to the concentrations where

* McBain's argument for the existence of two types of colloidal particle was based on other data, and is referred to in the last section.

²⁷ Hartley and Robinson, *Proc. Roy. Soc.*, 1931, 134A, 20.

only a negligible fraction of them exist in simple form *) the equivalent conductivity of the paraffin-chain radical (u) will be given by

$$u = \sum_p x_p l_p \quad (2)$$

Now, if the fraction $(m_p \cdot n_p)/m_p$ be written as θ_p , the total concentration of free gegenions will be $\sum_p x_p \theta_p$, and the contribution of these to the equivalent conductivity will be $l_g \cdot \sum_p x_p \theta_p$ where l_g is the equivalent conductivity of free gegenions. The concentration of the gegenions present in the form of micelles of type P is $cx_p(1 - \theta_p)$, and as these have a mobility of L_p , which is *negative* for the gegenions, the contribution of the gegenions as a whole to the total equivalent conductivity, will be

$$v = l_g \cdot \sum_p x_p \theta_p - \sum_p [x_p(1 - \theta_p)l_p] \quad (3)$$

The total equivalent conductivity is, of course, the sum of (2) and (3), *i.e.*

$$\lambda = l_g \sum_p x_p \theta_p + \sum_p x_p l_p \theta_p \quad (4)$$

and the transport numbers are the quotients of (2) and (3) by (4). The conductivity and transport measurements are thus completely represented by these two equations. It will be convenient, however, to introduce average values of θ , l and $l\theta$ which will be given by

$$\bar{\theta} = \sum_p x_p \theta_p \quad (5)$$

$$\bar{l} = \sum_p x_p l_p \quad (6)$$

$$\bar{l}\bar{\theta} = \sum_p x_p l_p \theta_p \quad (7)$$

a - denoting a mean quantity. $\bar{\theta}$ measures the total degree of dissociation of gegenions. Equations (2) and (4) now become—

$$u = \bar{l} \quad (8)$$

$$v = l_g \bar{\theta} - \bar{l} + \bar{l}\bar{\theta} \quad (9)$$

$$\lambda = l_g \bar{\theta} + \bar{l}\bar{\theta} \quad (10)$$

If we were dealing with only one type of micelle, the mean values would be single values and, therefore, $\bar{l}\bar{\theta}$ would be equal to the product of \bar{l} and $\bar{\theta}$. In general, however, this will not be true, and it will be useful for the purpose of analysis to separate the effects of change of average properties from change of "diversity" or "fluctuation" about the average. This can be done by introducing a function χ , defined by the equation

$$\bar{l}\bar{\theta} = \chi \cdot \bar{l} \cdot \bar{\theta} \quad (11)$$

which represents specifically the effect of this fluctuation, χ being unity for zero fluctuation and greater or less than unity according to the way in which the fluctuations of l and θ are related. Substitution of (11) in (10) gives us

$$\lambda = l_g \bar{\theta} + \chi \cdot \bar{l} \cdot \bar{\theta} \quad (12)$$

and of (11) in (9) gives

$$v = l_g \bar{\theta} + \bar{l}(\chi \bar{\theta} - 1) \quad (13)$$

* Strictly, this treatment is in any case quite general because one kind of "micelle" can be considered to be the simple paraffin-chain ion and another kind the simple ion-pair.

Solving (12) and (8) for $\bar{\theta}$, we obtain

$$\bar{\theta} = \frac{\lambda}{l_0 + \chi u} \quad (14)$$

These equations are exact. It remains to be considered what conclusions may be drawn from them on certain assumptions.

III. Further Considerations of the Increase of Equivalent Conductivity with Concentration.

Consideration of equations (8) and (12) shows that the value of $d\lambda/dc$ can only be positive while du/dc is negative if dl_0/dc , $d\bar{\theta}/dc$ or $d\chi/dc$ are one, two or all positive. The first two possibilities, an increase with concentration in the mobility of the free gegenions, or an increase in their total degree of dissociation, are quite contrary to expectations based on a knowledge of simple electrolytes. One or both of these increases must occur, however, unless $d\chi/dc$ is not only positive, but sufficiently great for $d(\chi u)/dc$ to be positive.

Now, in cetane sulphonic acid, from 0.046*N* to 0.162*N*, v (which interchanges throughout with u for cases where the paraffin-chain has an anionic end group) decreases by 32 per cent., χ would, therefore, have to increase by 46 per cent. even to maintain λ constant, and if neither $\bar{\theta}$ nor l_0 decreased. To produce the observed rise of λ by 18 per cent., the increase of χ would have to be much greater still. Even if the function χ changes in the desired direction, is a change of this magnitude at all probable?

It is evident, from the definition of χ (equation (11)), that, if the l and θ values of the various micelles were *entirely* independent, χ would be unity. The variations will not, however, be entirely independent. If another gegenion attaches itself to a micelle which suffers no other change, *both* l and θ will be decreased, and approximately proportionally, since the radius of the micelle is not appreciably altered. If another paraffin-chain ion enters while the number of gegenions remains the same, we shall have an increase of θ . The charge of the micelle will be increased, relatively, much more than its radius, and l will, therefore, be increased also. Since the volume of the micelle will consist almost entirely of paraffin-chain ions, it will be proportional to m and its effective radius, therefore, to $m^{1/3}$, while its charge will be given by $m\theta$. We shall, therefore, have, roughly, $l \propto m^{1/3} \cdot \theta$, and the second change of composition mentioned, since it increases m and θ , will give an increase of l relatively greater than that of θ . Addition or removal, however, of ions of either kind independently of the other, will not occur to any considerable extent. If m increases without increase of n , the potential at the surface of the micelle will increase and gegenions will, therefore, close in on the micelle and an increase of n with consequent decrease of θ is almost certain to follow. Similarly, a decrease of m will result in an increase of θ . For micelles of essentially the same type, i.e. micelles formed by aggregation of the paraffin chain ions in some definite state (isotropic liquid, nematic liquid, crystalline solid, etc.), the tendency will be for a certain constant potential to be maintained. Potential and mobility are approximately proportional, both being approximately proportional to $m^{1/3} \cdot \theta$, and hence the *tendency* will be for l to have a constant value for all the micelles of the same fundamental type at any one concentration,

just as the much larger particles of an ordinary colloid have mobilities almost independent of size.

On the whole, therefore, what variations of l and θ occur will be symbatic, *i.e.* we are more likely to find the high l values among the high θ values than among the low ones, and the low l values among the low θ values than among the high ones. Variation of this type will make the high values relatively more important in the $l\theta$ products than in l and θ separately, so that the mean of the products will be greater than the product of the mean values, *i.e.*, χ will be > 1 . Since, however, l will vary less than θ , the difference of these mean values will be less than it would be if l varied proportionally with θ , *i.e.*, χ will be $< \bar{\theta}^2/(\bar{\theta})^2$.

We should not be justified in attempting any statistical treatment of the θ variations until we know far more than at present about the forces involved. We think, however, that it will be generally agreed that the case where one-third of the micelles have θ values equal to the mean, one-third values half as great, and one-third values one-and-a-half times as great, though of a very artificial kind, represents far greater fluctuation than is at all likely to occur. For this case,

$$\bar{\theta}^2/(\bar{\theta})^2 = \frac{1}{3}\left[\left(\frac{1}{2}\right)^2 + 1^2 + \left(\frac{3}{2}\right)^2\right] = 7/6.$$

The extreme probable limits of χ are thus seen to be very close together, the lower limit being 1 and the upper limit being almost certainly < 1.1 .

Increase of χ by more than 46 per cent. is thus quite out of the question if we have micelles of fundamentally a single type.

Can the possible existence of two fundamentally different types of micelle enable us to avoid the conclusion that $d\bar{\theta}/dc$ (or dl_e/dc) is positive? Suppose we have two types, A and B. We shall distinguish quantities pertaining to each by suffixes a and b , and denote the fraction of paraffin-chain ions in the form of B micelles by y . We shall consider that it is the B micelles which increase at the expense of A micelles as the concentration increases (*i.e.*, dy/dc positive). In place of (8) and (12) we shall now have

$$u = l_a \cdot (1 - y) + l_b \cdot y \quad (15)$$

and

$$\lambda = l_e \bar{\theta} + \chi_a l_a \bar{\theta}_a \cdot (1 - y) + \chi_b l_b \bar{\theta}_b \cdot y \quad (16)$$

Now, if we are to avoid assumptions of the same kind of apparent improbability as positive values of $d\bar{\theta}/dc$ and dl_e/dc , we must assume not only these quantities to be negative, but all $d\bar{\theta}/dc$ and dl/dc values to be also negative and $\bar{\theta}_b$ to be $< \bar{\theta}_a$.

If we write

$$G = l_e \bar{\theta} + l_a \bar{\theta}_a (1 - y) + l_b \bar{\theta}_b y \quad (17)$$

then, since the χ values must be between 1 and $\chi_{\max.}$, where $\chi_{\max.}$ is their highest possible value, we have

$$\lambda > G \quad (18)$$

and

$$\lambda < \chi_{\max.} \cdot G - (\chi_{\max.} - 1) l_e \bar{\theta}. \quad (19)$$

Differentiating (17) with respect to concentration,

$$\frac{dG}{dc} = l_e \frac{d\bar{\theta}}{dc} + \bar{\theta} \frac{dl_e}{dc} + \bar{\theta}_a \frac{d}{dc} [l_a (1 - y)] + \bar{\theta}_b \frac{d}{dc} (l_b y).$$

the aggregates are essentially liquid,¹⁵ and since they will tend to present the minimum surface (which cannot consist entirely of "heads") to the water, they will presumably be roughly spherical and of the largest radius consistent with none of the "heads" being submerged in the paraffin interior. The radius of the paraffin centre will be slightly less than the length of a single fully-extended chain. For a chain of 16 C atoms this length will be about 19.2 Å, and the radius of the paraffin centre can, therefore, be taken as about 18 Å. From the volume of this, and taking the density to be that of liquid cetane (0.77), we can obtain the number of cetyl chains contained, which comes to about 50. In calculating the mobility of this micelle, we must make some allowance for the effective thickness of the ionic "heads" for which we may allow about 3 Å. The Stokes' law (without atmosphere effect) equivalent conductivity of paraffin-chain ions in this micelle at 35° C. will be $276 \times \bar{\theta}$, $\bar{\theta}$ having the significance previously described.

Let us take the case of cetyltrimethyl-ammonium bromide at a concentration of $N/50$. λ is = 33, and $u = 53.5$. If we assume l_0 to be reduced by about 25 per cent. by atmosphere effects, its value becomes 71. Taking a probable value for $\chi = 1.05$, and substituting in equation (14), we obtain $\bar{\theta} = 0.26$. The average charge on the micelle is, therefore, $50 \times 0.26 = 13$, and the solution is, therefore, to be considered as a 1.13-valent electrolyte of concentration $0.02 \times 0.26 = 0.0052N$. For this the value of $1/\kappa$ (the thickness of the atmosphere in the simple Debye-Hückel theory) comes to 16 Å. a , the distance of closest approach of the centres of a micelle and a gegenion, can be taken as 22 Å. Now, according to the simple Onsager assumptions, the "endosmotic" contribution to the equivalent conductivity of the micelle would reduce it to $\frac{1}{1 + \kappa a}$ of its Stokes' law value.⁹ The Stokes' law value is $276 \times 0.26 = 72$, and this would, therefore, be reduced to 30 instead of the observed 53. Although the reduction predicted by the simple theory is probably too great, reduction from 72 to 53 only by atmosphere effects is probably too small. We shall probably have, therefore, a higher value for $\bar{\theta}$ which can only be obtained by taking a lower value, say 50, for l_0 . This would give us $\bar{\theta} = .31$, valence of the micelle = 15.5, $1/\kappa = 13.5$ Å, and a Stokes' law value of $u = 86$. The latter would be reduced by the endosmotic term of the simple theory to 33. The observed reduction to 53 is now probably not too much less than that which the simple theory predicts.

Taking, now, the figures for the $N/10$ solution, we have $\lambda = 29$, and $u = 40$. If l_0 is now further reduced to, say, 40, $\bar{\theta}$ becomes 0.35, valence of micelle = 17.5, $1/\kappa = 5.4$ Å, and Stokes' law value of $u = 97$. The latter would be reduced, according to the simple theory, to so low a figure as 19, and it is not, therefore, surprising that the observed value of 40 is less than in the $N/50$ solution despite the increase of Stokes' law value consequent on the re-liberation of some of the adherent gegenions.

The least satisfactory feature of these calculations is the low values of l_0 which have to be assumed in order to avoid an improbably small value of the atmosphere reduction of micelle mobility. Until we have a satisfactory theoretical method of estimating the velocities of small ions near to large and highly-charged ones, it would not be useful to discuss the ways in which this difficulty could be avoided, except to mention that the assumption of a still larger micelle (which would have

to be ellipsoidal) is one of them. As Henry²⁸ has pointed out, a correction to the Stokes' law equation should be made for large particles which are internally non-conducting: for sufficiently large particles, this correction replaces the 6 in the denominator of the Stokes' expression for velocity by 4: this is in the right direction to reduce our difficulty, but it does not seem probable from Henry's calculations that our micelles are sufficiently large for the correction to be important.

It is hoped that, when accurate thermodynamic data are available for the dilute solutions, the size of the micelle may be more definitely estimated. Since the micelles will exert but little osmotic effect, the osmotic pressure, freezing-point depression, etc., will be due mainly to the free gegenions. There will, of course, be a considerable influence of ionic atmospheres which, however, can probably be more confidently estimated than the influence on the mobilities. If the osmotic coefficient, due to atmosphere effects, is g , then the observed van't Hoff factor, i , will be equal approximately to $g\bar{\theta}$. It is of interest to note that McBain, Laing and Titley²⁴ found the value of i , at 0° C., in the most dilute solutions of potassium oleate which they investigated, namely 0.2 N , to be 0.32. This is quite comparable with the value which we found probable for $\bar{\theta}$ at 0.1 N , in the case of cetyltrimethylammonium bromide. Work on other salts is in progress, and we hope to obtain more definite information also from comparison of the behaviour of salts having gegenions of different mobility and valence.

Finally, we may refer to the question of whether there is any conclusive evidence for the existence of more than one type of micelle. The fundamental argument by which McBain²¹ concluded that two types must be present, rested on the comparison of conductivity, transport and freezing-point data. It may be very conveniently expressed in terms of the general equations derived above. If we assume, as McBain did, that atmosphere effects are negligible, we can substitute i for $\bar{\theta}$ in equation (14), and take l_0 to have its value at infinite dilution. We may then calculate the value of χ . Taking values obtained directly, or by interpolation, from the work of McBain and collaborators,^{21, 24} we have, for potassium oleate at 0.2 N , $\lambda = 33.3$, $T_{01} = 0.78$ (both at 18° C.) and $i = 0.32$ (at 0° C.), whence χ must be = 1.5. At 0.5 N , $\lambda = 37.0$, $T_{01} = 0.70$ (at 18° C.) and $i = 0.32$ (at 0° C.), whence χ must be 2.3. If we have χ values really as high as these, the l and θ values of the various micelles present must be symbatic, and the variations must be so great that they could only be accounted for by micelles of fundamentally different types existing together, "ionic micelles" having high l and θ values, and "neutral colloid," having very low values of l and θ . Several factors, however, make the argument inconclusive. In the first place, there is a discrepancy in temperature between the measurements. i is known to increase with temperature,²⁴ and, if it is only 10 per cent. higher at 18° C. than at 0° C., the values of χ become 1.1 and 1.8, so sensitive are they to the value of i . In the second place, the atmosphere effects must be considered. We should replace $\bar{\theta}$ in (14) by i/g rather than i , and assign to l_0 a much lower value than that at infinite dilution. If we took the latter to be 40 for 0.2 N and 30 for 0.5 N in place of the infinite dilution value of 65, we should *increase* considerably the values of χ , but it would only be necessary for the values of g to be 0.71 and 0.51 respectively for χ to be reduced to 1.05, a value which it could have

²⁸ Henry, *Proc. Roy. Soc.*, 1931, 133A, 106.

if only one type of micelle were present. Such values of g are by no means inconceivable. If we apply the extended formula of Debye and Hückel,²⁹

$$1 - g = - \frac{1}{4\pi a^2 \sum n_i} \left[\log_e (1 + \kappa a) - \frac{\kappa a}{2(1 + \kappa a)} - \frac{\kappa a}{2} \right] \quad (15)$$

where $\sum n_i$ is the total number of charged particles per c.c., to evaluate g for the case of a 1-20 valent electrolyte having an " a " value of 20 Å, we obtain the values of 0.68 and 0.77 for 0.1*N* and 0.25*N* solutions, these concentrations being taken because they will be nearer to the effective concentration of the soap solution, which is the stoichiometric concentration multiplied by $\bar{\theta}$. In an attempt to estimate more correct values for the various coefficients than the simple Debye-Hückel theory is likely to give, one of us (G. S. H.)³ came to the conclusion that the correct values for g are probably *higher* than those given by equation (15). His calculations, however, were not made for higher concentrations than $N/100$, and it would, indeed, be quite worthless to attempt at present any computations for concentrations as high as those for which data are at present available. It is well to appreciate how concentrated these solutions are: the micelles carrying the enormous charge of perhaps 30, are about 40 Å in diameter and their mean distance apart, centre to centre, is only about 58 Å in the 0.5*N* solution. The application of the Debye-Hückel theory to such a system can only at present leave us with enormous uncertainty. These calculations have been introduced here chiefly to show how very much more seriously than is sometimes realised * the considerations of "atmosphere" effects can influence the quantitative arguments, and to show that the simple picture of these solutions derived from consideration of the causes underlying their peculiar behaviour is probably quite adequate to explain all the measured properties. If any evidence is to be conclusive on this question of the existence of more than one type of colloidal particle, it must depend on properties uninfluenced by coulomb forces. It is hoped in the near future to present results of measurements of some such properties.

²⁹ See Falkenhagen, *Elektrolyte*, 253 (Leipzig, 1932).

* McBain has frequently expressed the opinion^{17, 20, 21} that, since the charges on the surface of the micelle are far apart (the mean distance apart of thirty free charges on a micelle of radius 20 Å is about 13 Å, which is rather greater than the mean distance apart of like ions in a 0.75*N* solution of a uni-uni-valent electrolyte) the charge of the micelle is not a concentrated one, and the atmosphere effects, therefore, likely to be little greater than in a simple electrolyte. This argument has not been supported by any detailed considerations. As far as the atmosphere of the micelle as a whole is concerned, the charge, since it will be uniformly distributed, can be considered to behave *as though* concentrated at the centre. The size of the micelle is then fully allowed for by considering the atmosphere to extend inwards only up to a shell 20 Å away from this centre: it is true that the field of force here is no greater than near some simple ions, but it is *much more extensive*, both radially and tangentially, and detailed considerations³ show that this leads to the existence of enormously greater atmosphere effects. Now it is true that, near the micelle, the atmosphere will be localised around the individual ions in the surface, but the effect of this will be *added* to that of the micelle as a whole. The effect of the centre of the micelle having a very low dielectric constant can again only increase the effects above what is predicted assuming only the dielectric constant of water to be relevant.

³⁰ McBain, *J. Amer. Chem. Soc.*, 1928, **50**, 1636.

Summary.

1. Measurements have been made of the equivalent conductivity and transport numbers of two salts with paraffin-chain cations, containing 16 C atoms in the chain with the cationic group at the end. The results of a few measurements on cetane sulphonic acid are also recorded, and data collected from the literature on soaps are given for comparison.

2. The transport number of the paraffin-chain radical rises very rapidly with increase of concentration in the range, commencing abruptly at about $N/1000$, where the total equivalent conductivity falls, and attains values considerably greater than unity. In the first part of this range the rise of transport number is so great that the equivalent conductivity of the paraffin-chain radical rises above its value at infinite dilution, a fact which provides conclusive evidence of the formation in this range of mobile micelles—aggregates of paraffin-chain ions.

3. That a *fall* of total equivalent conductivity occurs when the micelles form is due to their great depressant effect on the mobility of the bromide ions, by causing some of these to adhere to them and exercising a braking influence on the others. The mean mobility of the bromide ions as a whole is negative over a considerable range of concentration.

4. The equivalent conductivity of the paraffin-chain radical reaches a maximum before the total equivalent conductivity has ceased its steep fall, and continues to fall while the latter is almost constant. In other paraffin-chain salts in which the total equivalent conductivity rises again in the moderately concentrated solutions, that of the paraffin-chain radical also falls. The rise of the total equivalent conductivity cannot, therefore, be due, as it has been thought to be, directly to replacement of less mobile simple ions by more mobile micelles. It is almost certainly due to the micelles, which have already been formed in much lower concentrations, re-liberating some of their attached gegenions. It does not seem necessary to assume the existence of more than one type of micelle.

5. Owing to the uncertainty of coulomb force effects of the Debye-Hückel type, it is not possible at present to draw any definite conclusions about the size of the micelles, except between limits so wide as to be hardly worth discussion, but roughly spherical micelles of about 20 Å radius, and containing about 50 paraffin-chain ions, whose existence is suggested by consideration of the forces operating in micelle formation, could not unreasonably explain the measured properties of the solutions.

One of us (B. C.) took part in this research at the suggestion of Dr. Conmar Robinson, and his contribution was made during the tenure of a Yuill scholarship of the University of Aberdeen, to whom our thanks are due. We are indebted to Dr. Robinson for the great interest he has taken in this work. Some of the work of C. S. S. was done during the tenure of a grant from the Department of Scientific and Industrial Research, for which we should also like to express thanks.

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PROPERTIES OF ILLUMINATED IODINE SOLUTIONS. PART II.—THE NEGATIVE ABSORPTION EFFECT IN BENZENE AND OTHER SOLVENTS.

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In a previous paper¹ we described the reversible *decrease* in the extinction-coefficient of illuminated iodine solutions in carbon tetrachloride and hexane caused by intense illumination and showed that this effect can be quantitatively accounted for by assuming a shifting of the equilibrium between I_2 molecules and I atoms, due to light absorption. We showed that in a number of solutions, including those of iodine in C_6H_6 , CH_3OH , and H_2O , and probably also that of bromine in CCl_4 , the effect has an opposite sign—the extinction-coefficient *increases* by illumination. We now describe some quantitative experiments made with benzene, and try to find an adequate explanation of the results obtained. The experimental arrangement was the same as that described in our previous communication.

Experimental Results.

Fig. 1 shows a set of measurements, made with a solution containing 4.0×10^{-4} gram molecules I_2 per litre of benzene. The ordinates are readings of the galvanometer, indicating the intensity of the light passing the absorption-cell filled with the solution; points indicate that the cell

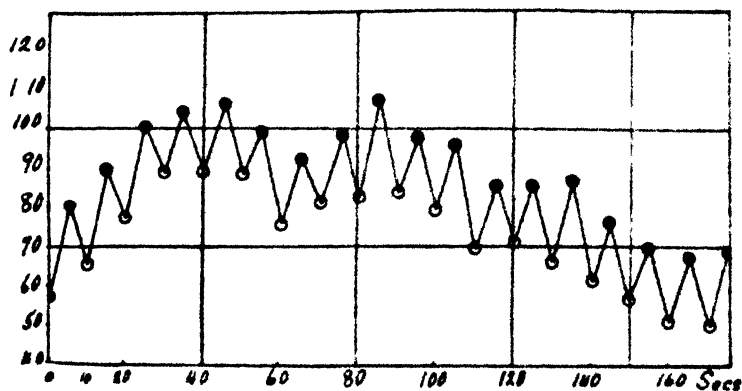


FIG. 1.

was kept in the dark, circles that it was uniformly illuminated by a 25 amps. carbon arc. The transmission is seen to be *smaller* during the illumination. The negative effect in C_6H_6 is about five times greater than the positive effect in carbon tetrachloride under the same conditions of concentration and light intensity (*cf.* Fig. 2 in Paper I.). At the highest light intensities used (5×10^{18} quanta absorbed per second in 1 c.c. of solution) the relative

¹ *Trans. Faraday Soc.*, 1936, **32**, 547.

change in the extinction-coefficient of the illuminated solution was of the order of 0.05 per cent.

(a) **Dependence of the Effect on Light Intensity.**—Table I. shows the results obtained, at constant I_2 concentrations, by variation of the intensity L of the illumination. A comparison of the last two columns of Table I. shows clearly that the negative effect is *proportional to the square root of the light intensity*—a rule which was found to hold in the case of the positive effect as well.

TABLE I.

Exp.	$c(I_2) \times 10^4$ mols./l.	L	ΔI	$\frac{\Delta I}{L}$	$\frac{\Delta I}{\sqrt{L}}$
100	4.0	44	— 22.7	0.52	3.42
		27	— 18.6	0.63	3.58
		17.5	— 16.2	0.93	3.88
		9.5	— 11.5	1.21	3.74
	8.0	32	— 16.7	0.52	2.96
		13.5	— 11.1	0.83	3.00
		9.0	— 8.2	0.91	2.73
	120	43	— 32.5	0.72	4.95
		25	— 25.8	1.03	5.16
		14	— 17.4	1.24	4.65
		9.5	— 14.1	1.48	4.57
		9.0	— 13.8	1.53	4.00

(b) **Dependence of the Effect upon the Concentration of Iodine.**—Since different concentrations mean different values I of the total light transmitted by the solution, we have to compare the *relative* changes of transmission $\Delta I/I$ corresponding to a given light intensity L . We use (in Table II.) for this purpose the mean values of $\Delta I/\sqrt{L}$ deduced from exp. 100 in Table I. The last two columns of Table II. indicate that the negative effect (in common with the positive effect) is proportional with the *square root* of the iodine concentration. The dependence of the effect on I_2 concentration is completely accounted for by the corresponding change in absorption, since the number of quanta absorbed is roughly proportional to the concentration. For a constant number of quanta absorbed the effect is *independent of the iodine concentration*.

TABLE II.

$c(I_2) \times 10^4$	$\frac{\Delta I}{\sqrt{L}}$	I	$\frac{\Delta I}{I\sqrt{L}}$	$\frac{\Delta I}{I\sqrt{L}c}$
4.0	3.66	7.4	0.12	0.25
8.0	2.90	3.9	0.09	0.26

(c) **Influence of the Wave-Length of the Illuminating Light.**—Experiments were made with the three sets of filters described in Paper I. which properties are given in Table III. The extinction-coefficients for set 2 and, especially, set 1 are somewhat higher than in the case of the iodine solution in CCl_4 (470 and 750 instead of 325 and 625) corresponding to the differences

in the extinction curves of these two solutions. The results obtained in these three spectral regions are given in Table IV. The last column shows

TABLE III.

Filter-Set.	Region.	$\bar{\lambda}^*$.	$\bar{\epsilon}^*$.
1	4000-5000 Å.	4700 Å.	470
2	4000-5500 Å.	5000 Å.	750
3	5000-5800 Å.	5700 Å.	550

TABLE IV.

$\bar{\lambda}$.	L .	ΔI .	$\Delta I \sqrt{\frac{\bar{\lambda}^*}{L \epsilon^*}}$.
4700 Å.	10	6.4	6.4
5000 Å.	32	16.7	7.6
5400 Å.	30.5	13.4	7.9

$\bar{\lambda}^*$ and $\bar{\epsilon}^*$ are the mean wave-length and the mean extinction-coefficient of the illuminating light; $\bar{\lambda}$ and $\bar{\epsilon}$ (in Table V.) meaning the same quantities for the photo-cell light.

(d) **The Effect in Different Spectral Regions.**—The positive effect is due to the disappearance of a part of the I_2 molecules, and there is no reason to expect a dependence of this effect on the wave-length of the light used for the measurement of the extinction-coefficient. The negative effect, however, must be due to the formation of some light-absorbing substance during illumination; the extinction curve of this unknown substance may be very different from that of the original solution. We therefore experimented with a constant concentration of iodine, and the same illuminating light, but different light-filters in the path of the beam used for the measurement of the extinction. The results are collected in Table V. These measurements although very rough (because of the wide

TABLE V.

Filters.	λ .	$\bar{\lambda}$.	$\bar{\epsilon}$.	$-\Delta I$.	I .	L .	$\frac{\Delta I}{I\sqrt{L}}$.	$\frac{\Delta I}{I\bar{\epsilon}\sqrt{L}}$.
Cu(NO ₃) ₂ + Wratten No. 39	4000-4800	4400	350	20.0	6.2	40	4.95	1.41
Cu(NO ₃) ₂ + Jena BG 12	4000-4900	4500	400	25.1	7.0	46	5.30	1.32
Wratten No. 75	4800-5100	5000	1100	6.2	1.1	45	8.40	0.76
Cu(NO ₃) ₂ + Wratten No. 55	4900-5300	5200	800	27.4	8.3	30	6.00	0.75
Wratten No. 61	5200-5600	5400	575	15.7	14.1	32	1.97	0.34

spectral regions used) clearly indicate a *decrease* in the quantity $\frac{\Delta I}{I_0 \sqrt{L}}$ with increasing wave-length. If the negative effects were due to a simple *increase in concentration* of the I_2 solution (as the positive effect is due to a *decrease* in it), then this quantity must be constant. The result indicates therefore that the absorbing molecules produced by illumination are *different from those forming the original solution*.

We will call this unknown substance the "photo-complex." If the photo-complexes were formed from a material which does not itself absorb visible light (*i.e.*, if the negative and positive effects were not combined), then the numbers in the penultimate column of Table V. would be simply proportional to the extinction-coefficients of the photo-complex. The extinction-curve would be that shown in Fig. 2. Since it is more probable that the photo-complex is formed at the cost of the original absorbing substance, the extinction-coefficients shown in Fig. 2 must be augmented by certain values proportional to the extinction-coefficients of the original solution.** This uncertainty cannot, however, change the general shape of the extinction-curve shown in Fig. 2. The photo-complex thus differs from the original I_2 solution by its relatively stronger absorption on the short wave-length side of the absorption-maximum.

(e) **Dependence of the Effect on Benzene Concentration.**—Table VI. shows the effect as a function of the concentration of benzene in carbon tetrachloride as a "neutral" solvent. The first value in the last column is very uncertain, because the effect passes through zero near this concentration. The last three values indicate that the resulting effect

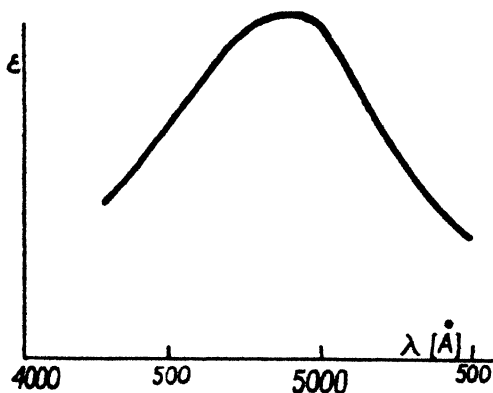


FIG. 2

TABLE VI.

$$c(I_2) = 8 \times 10^{-4} \text{ mols./l.}$$

$[C_6H_6]$ Vol. per Cent.	L	ΔI	$\frac{\Delta I}{\sqrt{L}}$	$\frac{\Delta I}{\sqrt{L} - 0.5}$ $[C_6H_6]$
0	41	+ 3.2	+ 0.5	—
2	27	+ 1.2	+ 0.23	(0.14)
16.7	34	- 1.2	- 0.17	0.040
50	33	- 6.3	- 1.10	0.032
100	32	- 16.7	- 2.90	0.035

** The factor of proportionality depending upon how many molecules of the photo-complex are formed at the cost of one molecule of the original substance.

is a linear function of the composition of the solution. In all probability, the negative effect by itself is simply proportional to the benzene concentration.

(f) **Effect in Benzene Vapour.**—No negative effect was observed in a mixture of iodine-vapour ($p = 0.16$ mm., corresponding to $c = 1 \times 10^{-4}$ mols./litre), with benzene vapour ($p = 75$ mm., corresponding to $c = 4.5 \times 10^{-3}$ mols./litre). This concentration is, however, still much lower than the smallest benzene concentration at which the negative effect was observed in solution ($c = 1.5$ mols./l).

(g) **Effects in Other Solvents.**—A negative effect of the same order of magnitude as in benzene was observed in a saturated iodine solution in water and in a solution of iodine in methyl-alcohol. A very small negative effect was observed in a *bromine* solution in carbon tetrachloride, but this result remains rather uncertain.

Discussion.

The following facts require an explanation :—

The occurrence of the negative effect.

Its proportionality with the square root of the light energy absorbed.

Its independence of the iodine concentration (other than that required by the foregoing point).

Its proportionality with the benzene concentration.

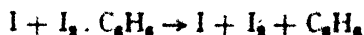
Two possible explanations are :—

(1) To assume the *dissociation by light of some complexes existing in the original solution*, and formation of free iodine, the process being reversed in the dark.

(2) To assume the *formation of complexes* (or increase in the concentration of already existing complexes), which dissociate again in the dark.

(1) **Dissociation of Complexes.**—This explanation is suggested by the fact that the negative effect is exhibited by solutions which are known to contain solvates ("brown" and "red" iodine solutions), and not by "violet" solutions in which the greater part, at least, of the iodine is in the form of free I_2 molecules. It is conceivable that these complexes absorb more strongly in the ultra-violet than in the visible region and their destruction may therefore lead to an increase in the extinction coefficients in the visible region.

The difficulties of this explanation are, however, very great : (a) The absorption-curve of the "photo-complex" appears, according to Fig. 2, to be different from that of "free" iodine. (b) The proportionality of the effect to the *square root* of the light intensity can be explained only on the assumption that the destruction of the complexes is achieved by iodine atoms, e.g., by a mechanism of the following kind :—

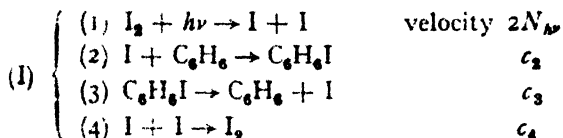


A mechanism of this kind is not impossible in itself, but the number of complexes destroyed during their life-time by iodine atoms must be proportional to the concentration of these complexes, and thus to the concentration (or some power of the concentration) of the iodine in solution, whereas the experiment shows no dependence of the effect on the iodine concentration. (c) In order to account for the order of magnitude of the effect, it is necessary to assume the formation of the complexes to be a *slow* process. The assumption that an activation energy is necessary for the formation of a solvate is, however, very unusual. The Van

der Waals forces, which are supposed to account for the formation of solvates, are purely attractive and cannot give rise to a potential barrier.

(2) **Formation of Complexes.**—The complexes in question can involve either iodine-atoms or molecules. In order to fulfil the square root law, the complexes must either be formed with a velocity proportional to the square root of the light intensity (and dissociate *mono-molecularly*), or with a velocity proportional to the first power of the light intensity (and dissociate *bi-molecularly*).

(a) The simplest conceivable hypothesis is that of a complex $C_6H_6 \cdot I$. If the following mechanism is adopted:—



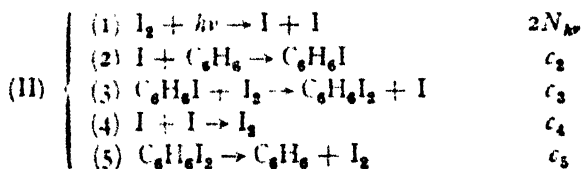
then the stationary concentration of the complex becomes:—

$$[C_6H_6 \cdot I] = \frac{c_2}{c_3} [C_6H_6] \sqrt{\frac{2N_{h\nu}}{c_4}} \quad . \quad . \quad . \quad (a)$$

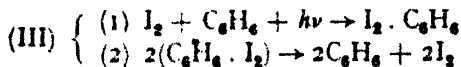
All the empirical rules are fulfilled, *viz.* proportionality to \sqrt{L} and $[C_6H_6]$, independence of $[I_2]$. This explanation, however, presents difficulty in the necessity of assuming that the complex $C_6H_6 \cdot I$ absorbs visible light, which is not absorbed either by C_6H_6 or by I atoms alone. Since *two* complexes $C_6H_6 \cdot I$ can be formed at the expense of *one* molecule I_2 , the molecular extinction coefficient of $C_6H_6 \cdot I$ must be greater than half the extinction coefficient of I_2 in order to account for the occurrence of the negative effect.

(b) In order to avoid the last-named difficulty, one may think of complexes involving I_2 , e.g., $C_6H_6 \cdot I_2$. To comply with the square root law these complexes ought either to be formed via iodine atoms, or dissociate bimolecularly:—

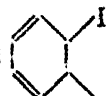
Either:




Or:



Reaction III (2) is difficult to justify. (II) is, however, not quite improbable. We may, for example, suppose that an I atom breaks

one double bond in C_6H_6 , and that a radical  is formed, which is capable of reacting with a molecule of I_2 .



The compound , which would then play the rôle of the "photo-

complex" can reasonably be supposed to be unstable and dissociate into C_6H_6 and I_2 . The stationary state, corresponding to the equation system (II) is

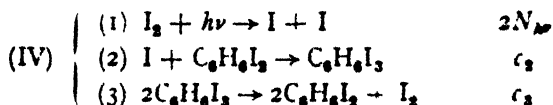
$$[C_6H_6 \cdot I_2] = \frac{c_2}{c_3 c_4} \sqrt{\frac{2N_{\text{av}}}{c_4}} [C_6H_6] \quad (b)$$

and agrees with all the observed relationships, just as in the case of (a).

It is, of course, possible for the photocomplex to be a "solvate" $C_6H_6 \cdot I_2$, instead of the molecule $C_6H_6I_2$; but it is then difficult to understand why iodine *atoms* should be necessary for its formation.

In any case, since one molecular complex can be formed at the cost of one free iodine molecule, the extinction coefficients of the complex in the visible region must be greater than those of iodine itself in order to account for the negative effect.

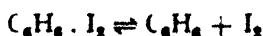
(c) The last possibility is that of complexes involving both iodine atoms and iodine molecules, *e g.*,



The stationary state is

$$[C_6H_6I_3] = \sqrt{\frac{2N_{\text{av}}}{c_3}} \quad (c)$$

and the effect must be independent of $[C_6H_6]$. Any attempt to introduce a dependence on $[C_6H_6]$ by assuming an equilibrium



simultaneously introduces a dependence on $[I_2]$, which is contrary to the experimental results.

The foregoing discussion shows that it is not easy to find a completely satisfactory explanation of the negative effect. Hypothesis (2a) involving $C_6H_6 \cdot I$ (or corresponding complexes of iodine atoms with other solvent molecules) appears to be the more probable of the two [(2a) and (2b)] which are consistent with the relationships deduced from the experimental results.

Summary.

Iodine solutions in C_6H_6 , CH_3OH , and H_2O , illuminated by the light from a 1500 watt carbon arc, show a reversible *increase* in their extinction coefficient during illumination. Exact measurements of this effect in a benzene solution show it to be proportional to the *square root* of light intensity, and independent of iodine concentration (for constant number of quanta absorbed). In I_2 solutions in CCl_4/C_6H_6 -mixtures, the effect is proportional to the concentration of benzene.

Two explanations are offered for the occurrence of this "negative" effect—one assuming a *destruction* of complexes (*e g.*, $C_6H_6 \cdot I_2$) by light,

the other the formation of new complexes (e.g., $C_6H_6 \cdot I$, or $C_6H_6 \cdot I_2$) during illumination. The first appears to be the more plausible, but the second is the only one which readily accounts for the above-mentioned experimental laws.

We heartily thank Professor F. G. Donnan, F.R.S., for his hospitality and for his kind interest in this work.

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KINETICS OF THE PARA-ORTHO HYDROGEN CONVERSION ON CHARCOAL.

BY R. BURSTEIN AND P. KASHTANOW.

Received 9th March, 1936.

In a previous communication¹ it was shown that hydrogen, adsorbed at high temperature on charcoal, decreases the activity of this catalyst to the *para-ortho* hydrogen conversion. The velocity constant shows a linear fall with an increase in the amount of the activatedly adsorbed hydrogen. While, however, with an adsorption of 0.2 c.c. of hydrogen (at 500° C.) the velocity constant of conversion decreases 30-40 times at room temperature (Fig. 1), it decreases only three times (Fig. 2) at the temperature of liquid air. A further increase in the amount adsorbed at high temperature affects the rate of conversion considerably less. The poisoning curve in the case of a conversion at 300° C. is similar to that at the temperature of liquid air (Fig. 3). To explain this phenomenon it may be assumed that centres which are not active at room temperature become active at the temperature of liquid air and at 300° C.

We shall here call these "centres of the second kind," as distinguished from those which are active at room temperature, which will be termed "centres of the first kind." The existence of two kinds of active points is also demonstrated by the shape of the poisoning curves in Figs 1 and 3.

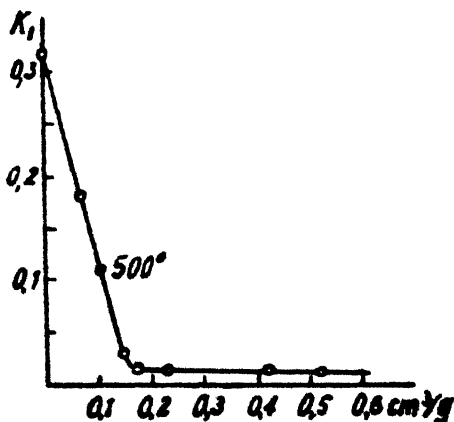


FIG. 1.—Conversion at 300° K., poisoned at 773° K., dynamic method. The ordinates are proportional to the reaction constant K , the abscissae indicate the amount of H_2 adsorbed.

¹ Burnstein und Kashtanov, *Acta Physic. Chem.*, U.S.S.R., 1934, 7, 465; *Nature*, 1934, 133, 571.

The half-period of conversion was calculated from the first order rate expression.

Figs. 1 and 3 show the data obtained in the experiments made by the dynamic method. The gas passed from a vessel through the catalyst during the time t . The pressure of the gas in the vessel containing the charcoal increased from 1×10^{-6} to a (approximately 40 mm.). The value of K_1 , which is proportional to the velocity constant, was calculated by the following equation—

$$K_1 = \frac{a}{t} \ln \frac{P_1 - P_\infty}{P_t - P_\infty}$$

where P_1 , P_t and P_∞ denote the *para*. H_2 percentage at the time $t = 0$, t , and $t = \infty$ i.e. in equilibrium.

Bonhoeffer, Farkas and Rummel,² in measuring the con-

version of hydrogen by the dynamic method, showed that the rate of conversion as a function of the

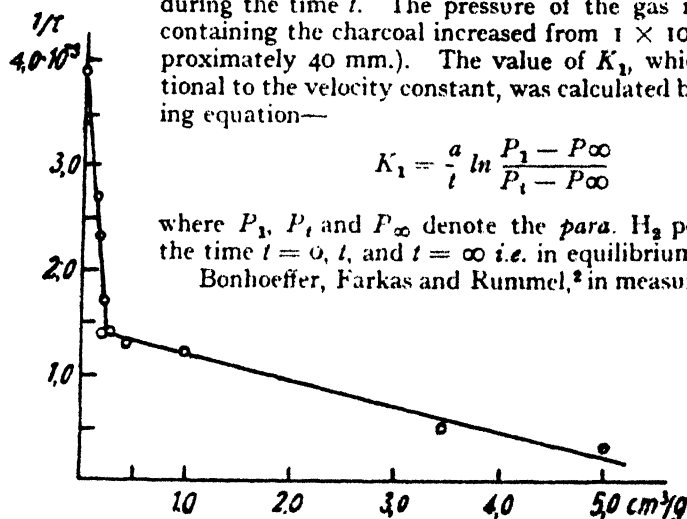


FIG. 2.—Conversion at 90° K., adsorption at 773° K. (static method).
Ordinates—reciprocal of half-time of the reaction

temperature is expressed by a parabolic curve. The minimum activity lies at temperature approaching room temperature, viz., at temperatures from 90° to 300° K. they observed a negative temperature coefficient, and above 300° K. a positive one.

In his further work Rummel³ measured the temperature coefficient by the static method within the range 63–106° K. and found the temperature coefficient of this reaction to be nearly zero.

The data obtained by the present writers in course of their previous researches showed different values of the temperature coefficients for pure and poisoned charcoal.

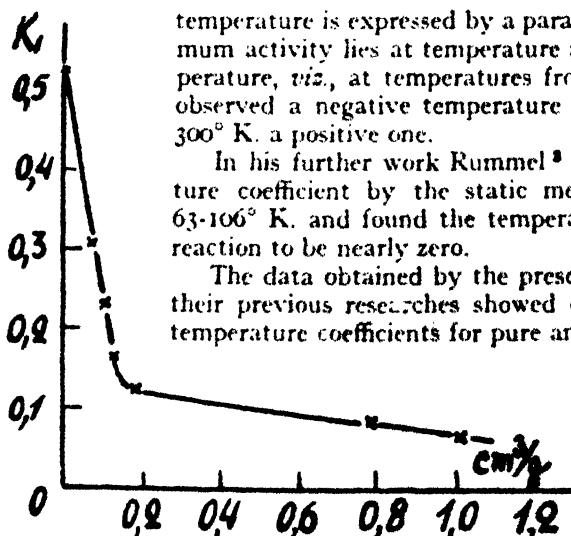


FIG. 3.—Conversion at 573° K., adsorption at 573° K. (dynamic method).

To investigate this point further, we have carried out a series of experiments with pure and poisoned charcoals by the static method within the temperature range of 20–90° K., and

by the dynamic method at 90 and 300° K. The latter experiments were made at atmospheric pressure.

² Bonhoeffer, Farkas and Rummel, *Z. physik. Chemie*, 1933, 21B, 225.

³ Rummel, *Z. physik. Chemie. A.*, 1933, 167, 221.

Experimental.

The experimental work was carried out in the same way as previously. The charcoal (5.5 g.) after being exposed to air was outgassed for forty-eight hours at 950°C ., and during the intervals between experiments again outgassed for twelve to fifteen hours. The charcoal was then cooled to the temperature of hydrogen adsorption, and after the adsorption of a definite amount of gas (at 500°C .) cooled again to the temperature at which the conversion was conducted. The influence of the amount of hydrogen, adsorbed at high temperature, upon the rate of conversion at 20°K ., 60°K .,* 77.5°K ., and 90°K ., was measured by the static method. In all of these experiments the same amount of hydrogen was taken for conversion; under normal conditions it was equal to 8 c.c. per gram of charcoal, and the pressure after complete adsorption did not exceed 2 mm.

To obtain a better cooling the vessel containing the catalyst was designed as shown in Fig. 4. In this vessel better cooling is obtained than in those previously used.

In the experiments conducted by the dynamic method the hydrogen was passed through the charcoal at the rate of 25 c.c. per minute. An hour after the beginning of the experiment, samples were taken for the measurement of the concentration. Measurements were made every fifteen minutes. In the experiments at room temperature and -80°C ., the hydrogen, before reaching the vessel containing the catalyst, was passed through a charcoal-filled tube which was immersed in liquid air. In this

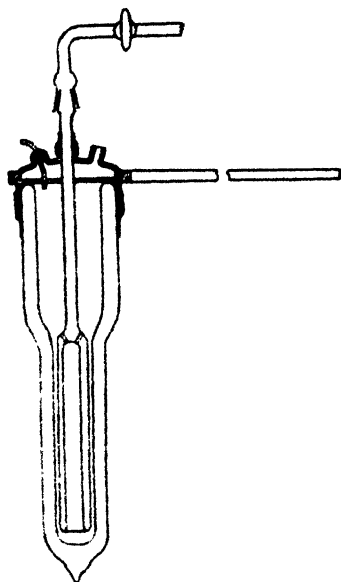


FIG. 4.

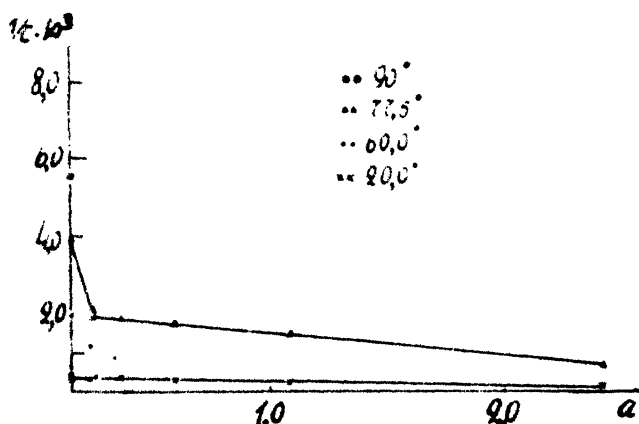


FIG. 5.—Conversion within the range of 20° – 90°K . Abscissae —amount of H_2 adsorbed in c.c./g. (static method).

tube a mixture of 47 per cent. of *para* hydrogen was obtained.

The experiments conducted by the static method showed that the velocity constant of the *ortho-para*-conversion increased with temperature, the activity of the centres, both of the first and the second kind, increasing.

* The temperature of 60°K . was reached by pumping out pure liquid oxygen to 5 mm.

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As seen from Table I. (Fig. 5), the activity of the centres of the first and second kinds are equally influenced by temperature.

Thus, *e.g.*, within the range of 60-77.5° K., the velocity constant on pure charcoal, *i.e.*, when centres of the first kind are present, increases about twice; in the case of poisoned charcoal (0.2 c.c. H./gr.), the conversion takes place only on centres of the second kind and the constant also increases twice.

TABLE I.

Temperature °K.	Hydrogen Absorbed at 500° C. in c.c./g.	<i>t</i> in Seconds	<i>K</i> ($\times 10^{-4}$).
20.4	0.0	2000	1.16
	0.0	2200	1.36
	0.23	2500	1.21
	2.51	5700	0.53
60	0.0	495	6.1
	0.206	1080	2.8
77.5	0.0	250	11.8
	0.23	520	5.78
	2.51	1470	2.06
90.0	0.0	180	16.8

The apparent energy of activation of this reaction in the range of 60-90° K. is about 350 calories for the active points of both the first and second kind.

In the experiments at 20° K. (Fig. 5) only centres of the second kind are observed. This fact may be possibly explained by a condensation of hydrogen at the most active spots of the first kind, the latter thus ceasing to take part in the conversion.

The results obtained by the present writers differ from those of Rummel, who has found the temperature coefficient of this reaction to be almost zero, while in the above experiments a positive, though small, temperature coefficient was observed both for the pure and for the poisoned charcoal (Fig. 6).

The experiments conducted by the dynamic method within the range of 90-573° K. have shown that the rate constant of this reaction on thoroughly degassed charcoal increases with temperature. Throughout this whole temperature range a positive temperature coefficient is observed.

On the other hand, in the case of a poisoned charcoal within the temperature range of 90-300° K., the *para-ortho*-conversion has a negative temperature coefficient, and within the range of 300-573° K., a positive one.

Fig. 7 and Table II.

give data expressing the relation between the rate constant and the temperature for pure (I.) and poisoned (II.) charcoal.

As it is very difficult to investigate the conversion at atmospheric pres-

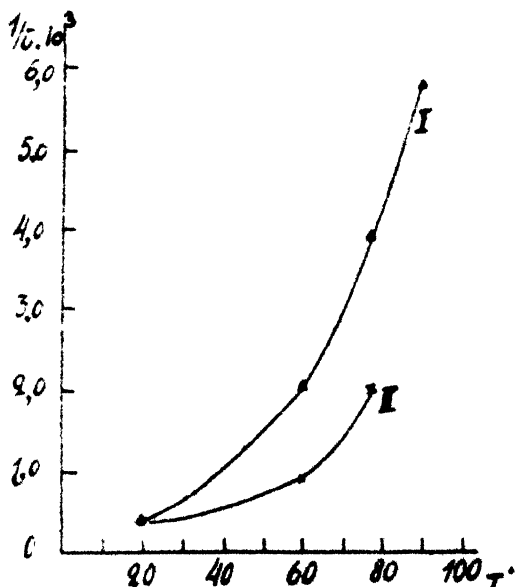


FIG. 6.—Increase of constant with temperature (static method). I. Pure charcoal. II. Poisoned charcoal.

sure and at 573° K., because the reaction is self-poisoned by the activated adsorption, the conversion was observed at 40 mm. Hg. The data obtained show that the velocity constant increases ± 1.5 -fold in the temperature range 293-573° K. on pure charcoal, and 5-fold on the poisoned charcoal. The

values in Table II. were calculated from these data.

With pure charcoal the apparent energy of activation calculated from experiments conducted by the static method is of the same order as that calculated from experiments made by the dynamic method. In the latter case the energy of activation throughout the whole temperature range (90-573° K.) varies from 130 to 409 calories.

We can obtain a better agreement between the values of the activation energy for active points of the first kind, calculated from the experiments using the dynamic and static method, if we subtract from the reaction constant of pure charcoal the reaction constant corresponding to the points of second kind. The energy of activation calculated in that way varies throughout the temperature range 90-573° K. from 460 to 210, whereas the static method gives 350 cal. in the range 60-90° K.

For the centres of second kind we find from the dynamic experiments—1300 cal. in the range 193-293° K., as against 350 cal. given by the static method of low temperature.

Generally speaking, the rate constant calculated from the results obtained by the static method may differ considerably from that obtained by the dynamic method. All the experiments made by the static method refer to a definite concentration of gas in

the surface layer, while those conducted by the dynamic method refer to a definite pressure.

The relation between the two values obtained for energy of activation can be explained as follows: The adsorption of hydrogen at room temperature is already sufficient to cover the centres of the first kind, so

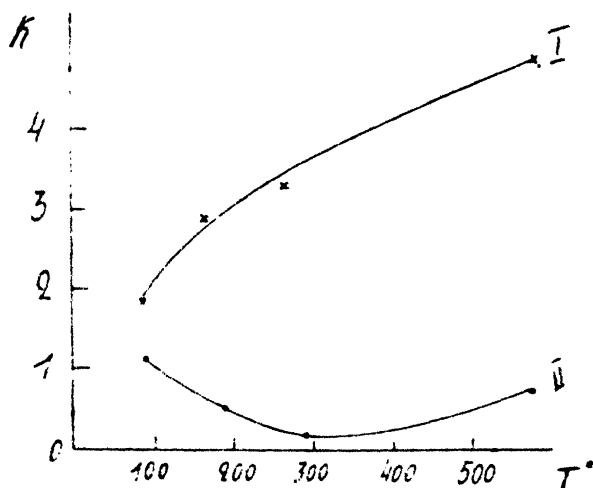


Fig. 7. Dependence of constant on temperature (dynamic method). I. Pure charcoal. II. Poisoned charcoal.

TABLE II

Temperature (°K.)	Amount of Hydrogen Adsorbed at 400° C. in cc. g.	K.
Pure charcoal.		
90	0.0	1.85
193	0.0	2.94
293	0.0	3.30
573	0.0	(calcul.) 4.62
Poisoned charcoal.		
90	0.45	1.23
193	0.41	0.51
293	0.41	0.16
573	0.37	(calcul.) 0.81

that the increase of adsorption with a fall of temperature does not affect the rate of the reaction. In this case the results obtained by the dynamic method become comparable with those obtained by the static method. The course of curve I. (Fig. 7) shows that throughout the whole temperature range studied the mechanism of the conversion is the same.

To explain the results obtained with active points of the second kind we have to suppose that, in this case, the concentration of hydrogen in the reaction space changes with temperature. As the heat of activation is much smaller than the heat of adsorption this accounts for the negative temperature coefficient. The data obtained by the present writers for poisoned charcoal are in agreement with those of Bonhoeffer.

The heat of adsorption being 1600 cal. and the apparent heat of activation — 1300 cal., we can calculate the true energy of activation which is 300 cal. This result is in good agreement with the data obtained by the static method, and with the value of the energy of activation on points of the first kind.

These considerations are correct if the reaction on the points of second kind is of the first order.

It is yet not quite clear whether the positive coefficient observed in the temperature range 300-573° may be connected with a new mechanism, as was supposed in similar cases by Bonhoeffer.

Summary.

On the surface of charcoal there are active centres of two kinds.

Experiments conducted by the static method have shown that the *ortho-para* hydrogen conversion on charcoal within the temperature range of 20-90° K. has a positive temperature coefficient. With a rise of temperature the activity of the centres of both the first and the second kind increases.

At 20° K. the centres of the first kind cease to be active. The apparent energy of activation of the *ortho-para*-conversion within the range of 20-90° K. is 350 calories.

Experiments carried out by the dynamic method with pure charcoal have shown that within the temperature range of 90-573° K. a positive temperature coefficient is observed. In similar experiments with poisoned charcoal within the range of 90-300° K. a negative temperature coefficient is observed, while within the range of 300-573° K., the coefficient is positive.

The study of the kinetics of the *para-ortho* hydrogen conversion on charcoal is being continued by the authors.

We are indebted to Professor A. N. Frumkin for the interest he has shown to this work, and to Professor L. V. Shubnikov who has afforded us the possibility of conducting experiments with liquid hydrogen at his laboratory in the Physico-Technical Institute.

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THE HOMOGENEOUS CATALYTIC OXIDATION OF BENZENE.

BY R. H. GRIFFITH AND S. G. HILL.

Received 12th March, 1936.

The oxidation of benzene in silica or porcelain bulbs was found by Fort and Hinshelwood¹ to be a homogeneous reaction in which relatively short chains played a part, and where the change was favoured by a high concentration of hydrocarbon. Newitt and Burgoyne² also showed that the non-catalytic oxidation of benzene under pressures of about 50 atm. at 280° and upwards was retarded by increased surface. In view of the fact that ethyl nitrate is known to have a marked effect on the spontaneous ignition temperature of aromatic hydrocarbons, and is of the type recognised by Ubbelohde and Egerton as pro-knocks, it appeared to be of interest to study the slow combustion of benzene in the presence of this catalyst.

The results which are now described are to be regarded as a survey of the conditions which exist in the presence of a vapour-phase catalyst.

Experimental Method.

The apparatus consisted of a Pyrex glass bulb of about 500 c.c. capacity, as shown in Fig. 1, heated in an electric furnace and connected to a source of purified oxygen and to an evacuation system and manometer. A small bulb C, of about 1 c.c. capacity, was used for admission of liquid benzene (analytical reagent quality) containing the desired amount of ethyl nitrate. The capillary connections and the manometer tube were heated to about 60°-65° by fine resistance wires up to the mercury level, in order to prevent condensation of liquid benzene. The change in total volume due to alteration in the manometer level was so small that it was neglected, and the system was regarded as one of constant volume. The course of the reaction was followed by determining the increase in pressure, and by subsequent analysis of the gaseous products. Typical curves are shown in Fig. 6, where it is clear that no induction

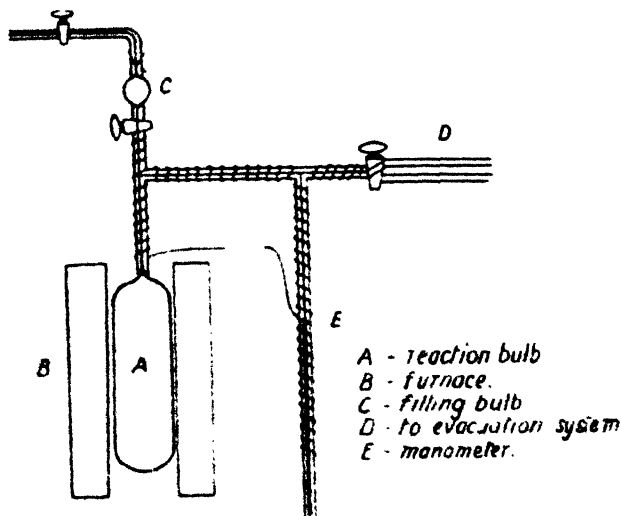


FIG. 1.

¹ *Proc. Roy. Soc., A*, 1930, 127, 218.

² *Ibid.*, 1936, 153, 448.

period was observed in any case. Newitt and Burgoyne² also found that no induction period appeared in the slow oxidation of benzene under pressure.

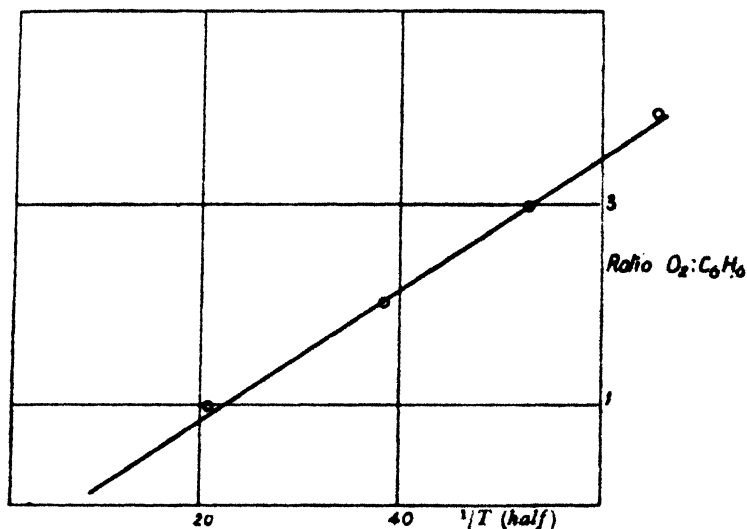


FIG. 2.

Initial pressure, 620 mm. Temperature, 433°.
 $EtNO_3 = 0.1$ per cent. on initial pressure.

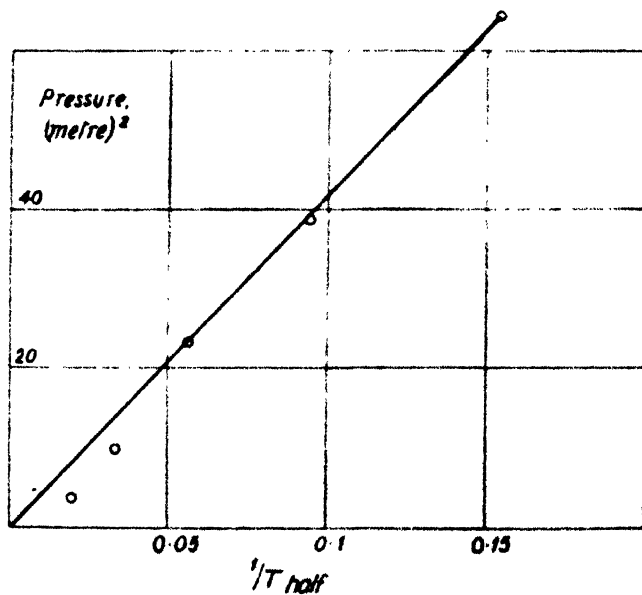


FIG. 3.

Ratio $C_6H_6 : O_2 = 1 : 1$. Temperature, 433°.
 $EtNO_3 = 0.1$ per cent. of initial pressure.

A standardised procedure was adopted in order to clean the bulb at the end of each experiment, so that the surface was in a similar condition before a new determination was carried out. The bulb was exhausted to

10^{-4} cm. at 450° or at any higher temperature which was investigated. The benzene in bulb C was then admitted to the reaction vessel, and the desired amount of oxygen, prepared from potassium permanganate and stored over 50 per cent. calcium chloride solution, was allowed to enter.

Results Obtained.

(a) **Ratio of Benzene to Oxygen.**—Experiments at 433° with an initial total pressure of 620 mm. and 0.62 mm. of ethyl nitrate (0.1 per cent. of initial pressure) were carried out to determine the effect of changes in the relative concentrations of benzene and oxygen. These are summarised in Fig. 2, where the time of half-change is seen to depend directly on the ratio



(b) **Pressure.**—

In Fig. 3, the influence of pressure is shown for an equimolecular mixture of benzene and oxygen at 433° , with ethyl nitrate equal to 0.1 per cent. of the total pressure. It will be seen that the reaction is approximately one of the third order, but probably of an even higher order at low pressures.

(c) **Temperature.**—The variation in the time of half-change with temperature is shown in Fig. 5, for a mixture of $C_6H_6 + 2O_2$, and ethyl nitrate 0.1 per cent. of the total initial pressure of 620 mm.

(d) **Concentration of Ethyl Nitrate.**—It was found that with a $C_6H_6 + 2O_2$ mixture at 433° , with initial pressure 620 mm., the time of half-change varied inversely as the concentration of ethyl nitrate. This is shown in Fig. 4, from which it was to be expected that the reaction with 0.35 per cent. or more of ethyl nitrate would be so rapid that the mixture would explode. This was found to be the case with both 0.35 and 0.4 per cent. concentrations.

(e) **Effect of Surface.**—Comparative experiments with the empty bulb and with a similar bulb containing Pyrex glass tubes which gave a

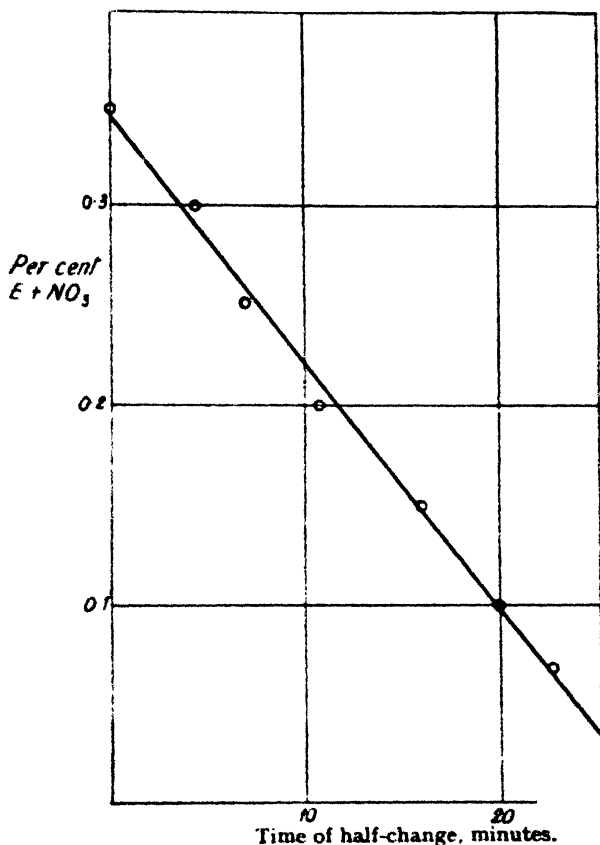


FIG. 4.

Temperature, 435° .
Pressure, 620 mm. initial.
Ratio $C_6H_6 : O_2 = 1 : 2$.

surface approximately ten times as great were done at 430° and 435° with benzene : oxygen = 1 : 2 and ethyl nitrate 0.1 per cent. of an initial total pressure of 620 mm. It will be seen from Fig. 6 that considerable retardation occurs which is slightly more pronounced at the lower temperature. It was also observed that slight decomposition of benzene which contained no ethyl nitrate took place in the packed bulb although it was not detected in the empty bulb.

(f) **Effect of Tetra-Ethyl Lead.**—The effect of simultaneous presence

of ethyl nitrate and tetra-ethyl lead is illustrated by Fig. 7, where it is clear that the oxidation is greatly suppressed by the addition of the knock inhibitor.

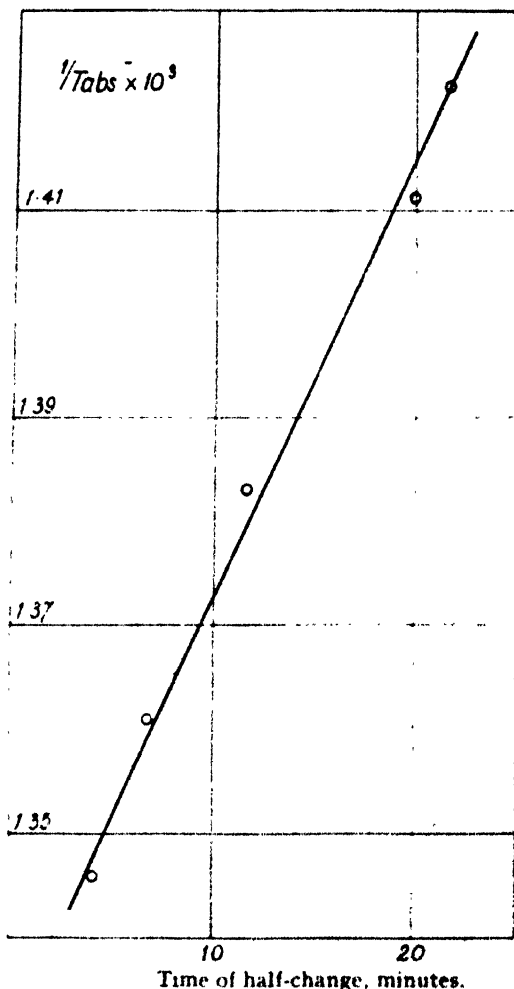


FIG. 5.

$C_6H_6 : O_2 = 1 : 2$.
 $EtNO_2 = 0.1$ per cent. of initial pressure.
 Initial pressure, 620 mm.

Composition of Reaction Products.

It was observed that although the increase in pressure reached a maximum and remained at that point for some time, a gradual decrease in pressure then set in and progressed slowly during very long times. This is probably due to polymerisation reactions which lead to the formation of diphenyl or diphenyl oxide, and a crystalline deposit was, in fact, observed on the walls of the bulb when cold. By washing the vessel with alcohol and diluting the washings with water, a solid was extracted and after recrystallisation it melted at 71° . The residue had the characteristic odour of diphenyl oxide, but there was no indication that phenol or diphenylene oxide were also present.

Gas samples were withdrawn from the hot bulb by way of a U-tube cooled in solid carbon dioxide mixed with acetone; this

retained any unchanged benzene or condensable products. The composition of the permanent gas is shown in Tables I. and II. for a variety of conditions. The varying content of nitrogen is accounted for by the small volume of air which was unavoidably present when bulb C was not completely filled with benzene.

TABLE I.—GASEOUS PRODUCTS FROM OXIDATION OF BENZENE.

(Effect of oxygen concentration at 433°, with 0.1 per cent. ethyl nitrate.)

	CO ₂	O ₂	CO	N ₂	Acetylene
C ₆ H ₆ + O ₂	30.9	2.3	63.9	2.9	++
2O ₂	38.0	0.9	58.3	2.8	+
3O ₂	42.7	4.9	49.8	2.6	+
4O ₂	46.5	5.7	45.0	2.8	—

(Initial pressure 620 mm., 0.1 per cent. ethyl nitrate, 2O₂ : 1C₆H₆.)

At 435°	38.0	0.9	58.3	3.2
450°	35.3	0.4	61.1	6.5
462°	31.9	0.9	64.4	6.2
470°	28.9	1.7	66.3	4.3

(At 450°, initial pressure 620 mm., 2O₂ : 1C₆H₆.)

EtNO ₂ 0.1 per cent.	35.3	0.4	61.1	3.2
EtNO ₂ 0.2 per cent.				
+ PbEt ₄ 0.1 per cent.	43.6	2.3	47.6	6.5
.. 0.33 per cent.	35.8	26.4	31.6	6.2

(620 mm. pressure, 0.1 per cent. ethyl nitrate.)

Packed bulb 430°	25.8	31.5	38.0	4.7	—
Empty	36.6	3.9	56.7	2.8	+
Packed .. 435°	32.6	21.0	41.5	4.9	+
Empty	38.0	0.9	58.3	2.8	+

TABLE II.—GASEOUS PRODUCTS FROM OXIDATION OF BENZENE.

(Effect of ethyl nitrate concentration on 2O₂ : 1C₆H₆ at 433°.)

Per Cent. EtNO ₂	CO ₂	O ₂	CO	N ₂	C ₂ H ₄	Unsat. Hydrocarb.	CH ₄	H ₂
0.07	43.1	0	54.8	2.1	—			
0.1	38.0	0.9	58.3	2.8	—			
0.25	36.5	1.0	58.5	2.0	++			
0.3	36.3	1.2	59.7	2.5	+++			
0.35	3.9	1.1	51.6	1.8	2.2	1.2	2.1	36.1 *
0.4	3.2	0.4	50.7	2.8	1.5	1.4	2.5	37.5 *

(Effect of total pressure : 1 : 1 mixture at 433°.)

	CO ₂	O ₂	CO	N ₂
310 mm. initial	27.0	0.1	68.2	4.7
480	30.4	2.3	63.7	3.6
620	30.9	2.3	63.9	2.9
800	31.6	1.3	64.2	2.9

* There was also a heavy deposit of carbon in these experiments.

Discussion.

The general characteristics of the catalysed reaction at 430°-480° are very similar to those of the uncatalysed reaction at 500°-530°. The catalyst acts as a chain initiator and its effect is counteracted by glass surface or by lead tetra-ethyl. The chains appear to be relatively short, but direct comparison with the uncatalysed reaction is not possible. The reaction approximates to one of third order, but the ethyl nitrate concentration affects the rate directly, so that the true order is one

lower. The fact that increase in the oxygen concentration leads to a decrease in reaction velocity agrees with the data of Fort and Hinshelwood on the uncatalysed reaction, and with the conclusions of Ubbelohde.³ The solid reaction products which have been isolated are similar to those

detected by Mead and Burk⁴ in the thermal decomposition of benzene.

The composition of the gaseous products shows several regular gradations; increase of oxygen leads to a higher CO_2/CO ratio, while a rise in the reaction temperature has the opposite effect. The presence of lead tetra-ethyl, or of additional glass packing in the bulb, gives a high residual concentration of oxygen. When the concentration of ethyl nitrate is increased, the ratio of CO_2/CO decreases slowly until explosion occurs, when a gas mixture of an entirely different type is formed, similar to that observed by Bone and Hill⁵ for the explosion of ethane. The influence of total

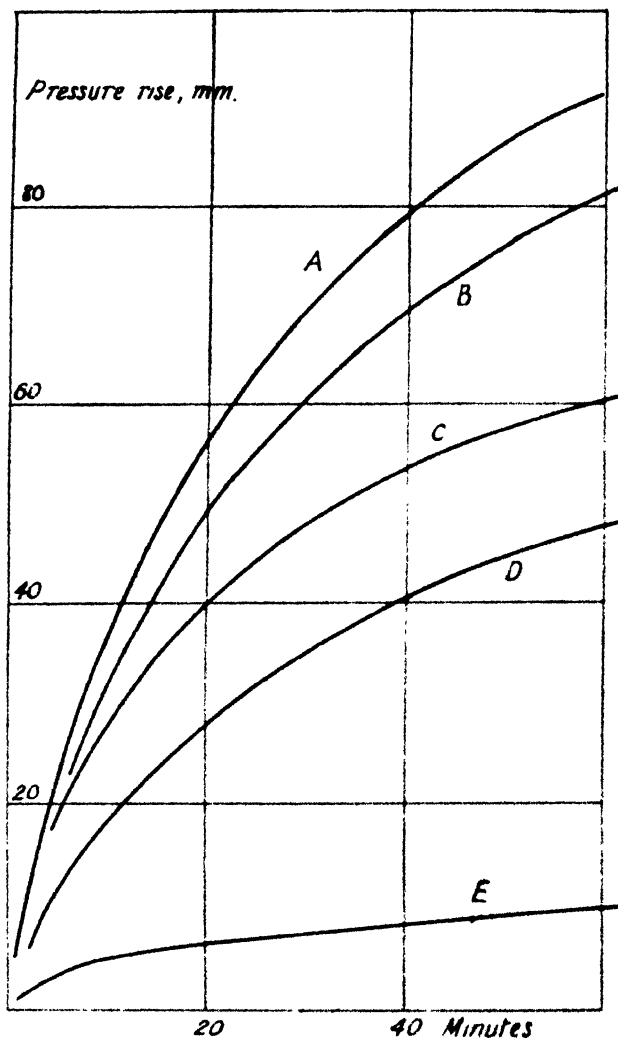


FIG. 6.

A = empty bulb at 435° . C = packed bulb at 435° .
 B = " " 430° . D = " " 430° .
 E = packed bulb without ethyl nitrate.
 Initial pressure, 620 mm.
 $\text{C}_6\text{H}_6 : \text{O}_2 = 1 : 2$, ethyl nitrate 0.1 per cent.

pressure on the composition of the gas is very small, and above 480 mm. is practically negligible.

³ *Proc. Roy. Soc., A*, 1935, 153, 354.

⁵ *Proc. Roy. Soc., A*, 1930, 129, 434.

⁴ *Ind. Eng. Chem.*, 1935, 27, 289.

The production of acetylene was observed in several instances, particularly with higher concentrations of ethyl nitrate.

The fact that phenol was not detected under these conditions, although it was formed in large yields in the experiments of Newitt and Burgoyne, is probably chiefly due to the higher temperatures employed in the present investigation, but may also be caused by the influence of the catalyst on the combustion of any phenol which is formed.

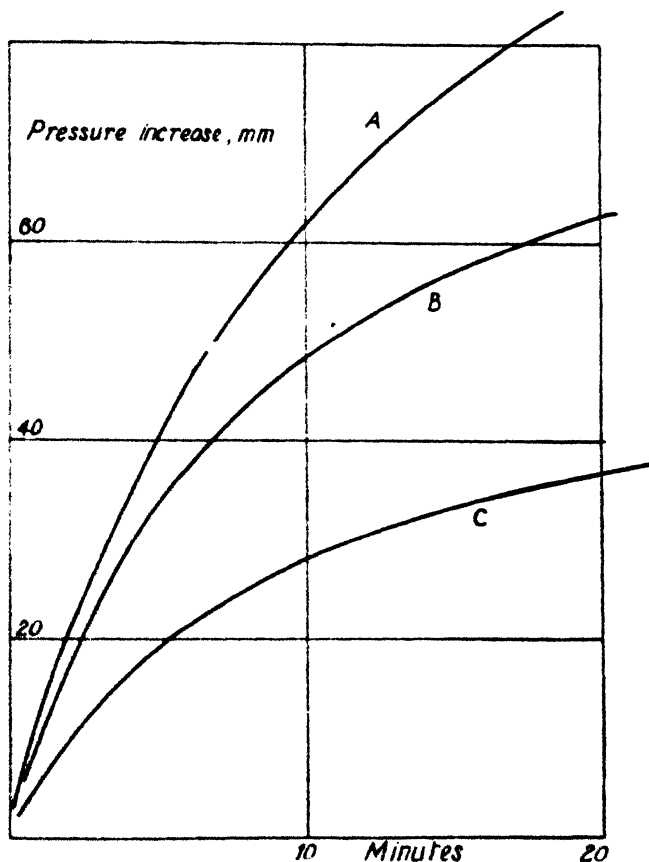


FIG. 7.

A = ethyl nitrate.

B = " " + 0.1 per cent. PbEt_4 .

C = " " + 0.3 " " "

Temperature, 450° .

Initial pressure, 620 mm.

$\text{C}_2\text{H}_5 : \text{O}_2 = 1:2$.

$\text{EtNO}_2 = 0.1$ per cent. of initial.

The Function of the Catalyst.

Ethyl nitrate conforms to the type of pro-knock anticipated by Egerton and Ubbelohde,⁶ but certain observations on its thermal decomposition do not supply evidence for the suggested mechanism. It was found that ethyl nitrate decomposed in the glass bulb at 435° giving, for example, a pressure increase of 106 mm. in 220 minutes from an initial

⁶ *Nature*, 1935, 135, 67.

pressure of 269 mm. The reaction products were withdrawn by way of a tube cooled in solid carbon dioxide, and contained

	NO	.	.	15.8
	CO ₂	.	.	10.4
	O ₂	.	.	0.5
Unsat. hydrocarbons		.	.	1.3
	H ₂	.	.	10.4
	CO	.	.	36.8
	CH ₄	.	.	10.8
	C ₂ H ₆	.	.	2.1
	N ₂	.	.	11.9

Acetylene was absent when tested by Schultz's reagent. Peroxides active to TiCl₄ were absent, and on the admission of air an immediate brown coloration due to nitrogen peroxide was produced. This resembles the results obtained by Steacie and Shaw ¹ for the decomposition of ethyl nitrite.

*Fulham Laboratory,
The Gas Light and Coke Company.*

¹ *J. Chem. Physics*, 1934, **2**, 435.

REVIEW OF BOOK.

Lehrbuch der Physikalischen Chemie. Vol. V, 2nd Section. By K. JELLINEK. (Stuttgart, Ferdinand Enke. Pp. 289-576 + 185 figs. 27 RM.)

This continuation of the monumental textbook of Dr. Jellinek treats mainly with the properties of the atom. It is the most physical of the sections that have appeared so far, and has probably been introduced into the textbook of physical chemistry because it will form the basis of the next section on molecular structure. Among the topics dealt with are mass spectroscopy, the scattering of α -particles, atomic spectra, and the Bohr and Sommerfeld theories, X-rays and their reflection by crystals, the theory of spectra including the Pauli principle, the Periodic Table, radioactivity and isotopes, inelastic collisions between nuclei and various projectiles and artificial radioactivity.

The present section maintains the good features of the earlier volumes and is very clearly written with full experimental and mathematical details throughout. It is an admirable work of reference if only for the facts it contains, but it is more than that, for the facts have been welded into a continuous story of very great interest. The section on the nucleus is especially valuable, since the author surveys the whole field in short compass, up to the present day.

The work is excellently printed, and to aid the non-mathematical reader the mathematical and more technical details are presented in small type.

W. E. G.

THE SURFACE ANALYSIS OF PARTICLES OF CERTAIN WHEAT FLOURS.

BY IAN KEMP.

Communicated by ERIC K. RIDEAL.

Received 18th February, 1936.

Wheat flour consists essentially of starch, proteins (of which gliadin and glutenin form the major part) lipoids and electrolytes. A suspension of flour will therefore consist of starch particles upon whose surfaces may be adsorbed proteins or lipoids. It is of importance in the colloid chemistry of flour to form some estimate of the *fractions* of the surfaces of the particles of starch which are covered with protein and with lipid.

For the estimation of the distribution of capillary active substances over the surface of a composite colloidal particle, it is necessary to select some additive surface property, and one of the more convenient methods is the measurement of the surface charge density on the particle by cataphoresis.

Thus, in the case of flour, if σ_p , σ_l , σ_s be the surface charge densities of the protein, lipid, and starch surfaces respectively, and f_p , f_l be the fractions of the surface of the starch particle covered with protein and with lipid respectively, then if we assume that the surface charge densities are additive, the resultant surface charge density of the flour particle is

$$\sigma = f_p \sigma_p + f_l \sigma_l + \sigma_s (1 - f_p - f_l) \quad (1)$$

In practice the cataphoretic mobility of particle is proportional to its surface charge density, the relation having been shown previously (Kemp)¹ to be satisfactorily expressed by the equation of Henry.²

$$\mu = \frac{\sigma}{\eta} \cdot \frac{ka}{1 + ka} f(ka) \quad (2)$$

where μ denotes the cataphoretic mobility, σ the surface charge density, η the coefficient of viscosity of the solution, a the radius of the particle, k is proportional to the square root of the ionic strength, and $f(ka)$ is a function of ka . According to this equation, the variation in mobility with particle size is negligible for the purpose of the present experiments when ka is greater than 100. Thus equation (1) can be written

$$(\mu - \mu_s) = (\mu_p - \mu_s) f_p + (\mu_l - \mu_s) f_l \quad (3)$$

where μ , μ_p , μ_l , μ_s are the mobilities of particles of flour, protein lipid and starch respectively, the particles being of similar size and the ka value not being much less than 100. The values of these mobilities are determined by the ionic environment, and hence by measuring the

¹ Kemp, *Trans. Faraday Soc.*, 1935, **31**, 1347.

² Henry, *Proc. Roy. Soc.*, 1931, **133A**, 106.

mobilities of the four types of particle in two different ionic environments, the values of f_p and f_i can be calculated from the equations :

$$(\mu' - \mu'_s) = (\mu'_p - \mu'_s) f_p + (\mu'_i - \mu'_s) f_i \quad (4)$$

$$(\mu'' - \mu''_s) = (\mu''_p - \mu''_s) f_p + (\mu''_i - \mu''_s) f_i \quad (5)$$

for the mobilities in the two cases.

It was therefore necessary to investigate the cataphoretic behaviour of proteins, lipoids and starch of flour, and finally of flour itself in suitable solutions. In practice the particles employed were never much less than 1μ in size and the ionic strength was 0.001, so that ka was about 100, and the effect of small variations in particle size upon the mobility could be neglected.

By such methods it was found possible to make some estimate of the amounts of proteins and of lipid on the surfaces of the starch particles in suspensions of flour.

1. Experimental.—Measurements of cataphoretic mobility were made with a microcataphoresis apparatus of the Mattson type. Measurements of hydrogen ion activity were made with the quinhydrone and glass electrodes.

2. Glutenin.—Samples of this protein from two sources were investigated, one having been prepared in the laboratory of the Research

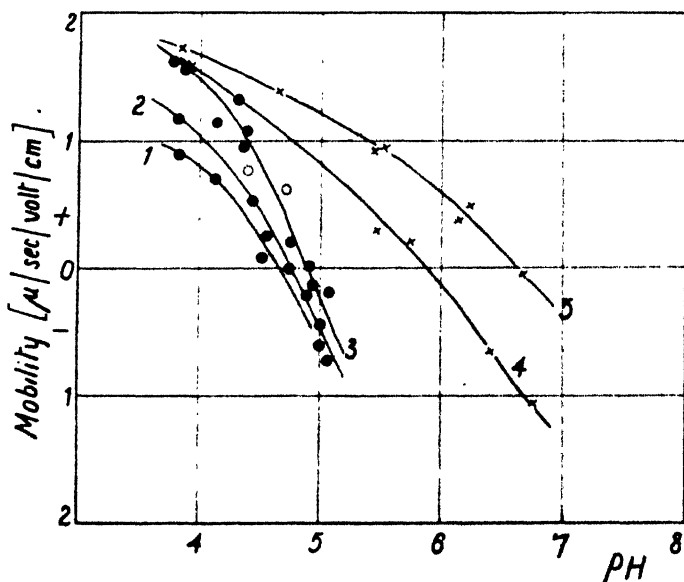


FIG. 1.—Curve 1 { Glutenin in acetate } 0.02 ● English sample.
 2 { buffers of constant } 0.01 ○ American sample.
 3 { ionic strength. } 0.001.
 4 { Gliadin in buffers } 4 After 4 days in 70 per cent.
 of ionic strength } alcohol.
 5 { 0.001 } 5 Untreated.

Association of British Flour Millers, and the other in the United States of America. The variation of mobility with ionic environment was determined for silica particles covered with glutenin and no appreciable difference between the two samples was noted. The detailed results are given graphically as Fig. 1.

The data regarding the isoelectric point are collected in Table I. The effect of excess anionic adsorption is clearly seen, and the isoelectric reaction at "infinite dilution" may be taken as p_H 4.90.

3. Gliadin.—In a previous publication (Kemp and Rideal) * the isoelectric point of gliadin was shown to be at p_H 5.10 in very dilute solutions. The sample of gliadin used had been allowed to stand in 70 per cent. alcoholic solution for some days before measurements were made.

In order to investigate the possibility of alcohol-denaturation having occurred, the isoelectric p_H of gliadin which had been dissolved in dilute acetic acid was determined. The sample of gliadin, which was prepared by the Research Association of British Flour Millers, was adsorbed on silica particles for the mobility measurements. The results are shown in Fig. 1, and it will be noted that the isoelectric reaction is p_H 6.60 \pm 0.05 in solutions of ionic strength 0.001 (curve 5). This value is in agreement with results of other workers. It is clear that, on standing in alcoholic solution, denaturation of the gliadin occurs, with the disappearance of basic groups. This was further corroborated by a measurement of the isoelectric reaction of a sample which had been allowed to stand in 70 per cent. alcohol for four days, when the isoelectric p_H had fallen to 5.92 \pm 0.05. The results are expressed as curve 4 of Fig. 1.

4. Natural Protein Mixtures.—The natural protein mixtures were isolated from flours by extracting the lipoids with petroleum ether, and removing the starch by kneading in a stream of water.

TABLE I.

Solution.	Ionic Strength at Isoelectric p_H .	Isoelectric Point.
Mixtures of N/10 .	0.043	4.50 \pm 0.03
" N/50 .	0.012	4.78 \pm 0.02
" N/100 .	0.008	4.94 \pm 0.03
" N/500 .	0.0013	4.90 \pm 0.05
Ionic strength 0.001 .	0.001	4.90 \pm 0.10
" " 0.01 .	0.01	4.70 \pm 0.05
" " 0.02 .	0.02	4.66 \pm 0.05

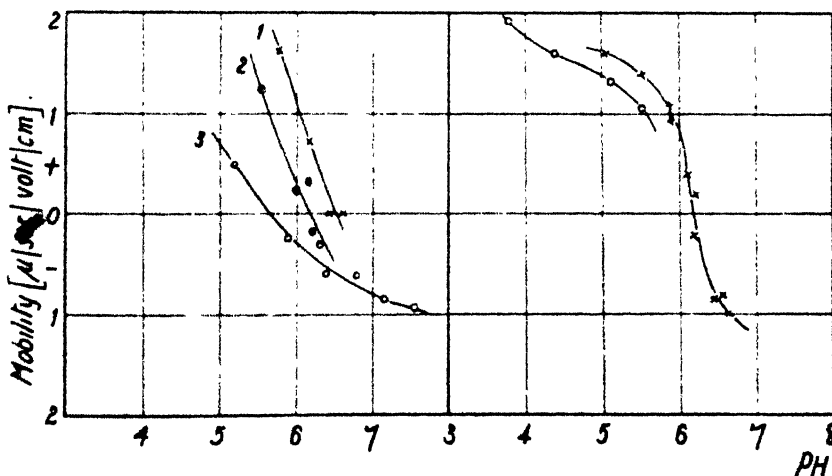


FIG. 2.—Natural protein mixtures from Manitoba flour.
Curve 1. Ionic strength 0.001.
" 2. Ionic strength 0.001 after 40 hours in 70 per cent. alcohol.
" 3. Ionic strength 0.02.

FIG. 3.—Natural protein mixture from English flour in buffer solutions of ionic strength 0.001.
× Phosphate buffers.
○ Acetate buffers.

* Kemp and Rideal, *Proc. Roy. Soc.*, 1934, **147A**, 1.

results that the surface gliadin-glutenin ratio is greater in Manitoba than in English flour.

It will be seen from Figs. 1, 2, and 3, that the electrophoretic behaviour of the protein mixture obtained by kneading ether-extracted flour is not

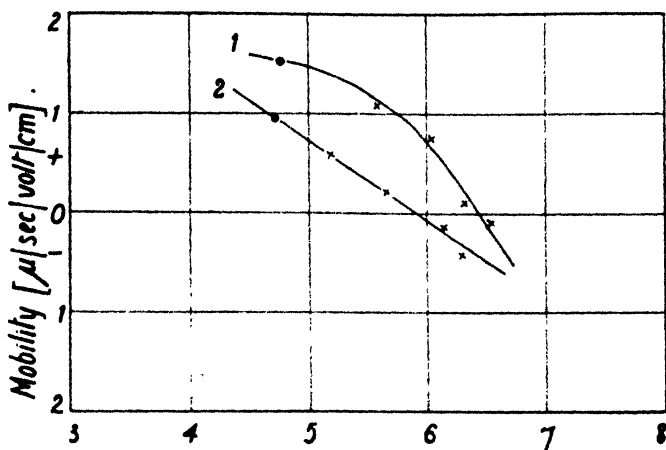


FIG. 6.—Gluten from English flour in solutions of ionic strength 0.001.

Curve 1. Untreated. × Phosphate buffers.
Curve 2. Heated to 90° C. for 6 hours. ● Acetate buffers.

completely explained by the behaviour of the two main constituent proteins, gliadin and glutenin. The difference may be due to the persistence of a lecithin protein complex after ethereal extraction.

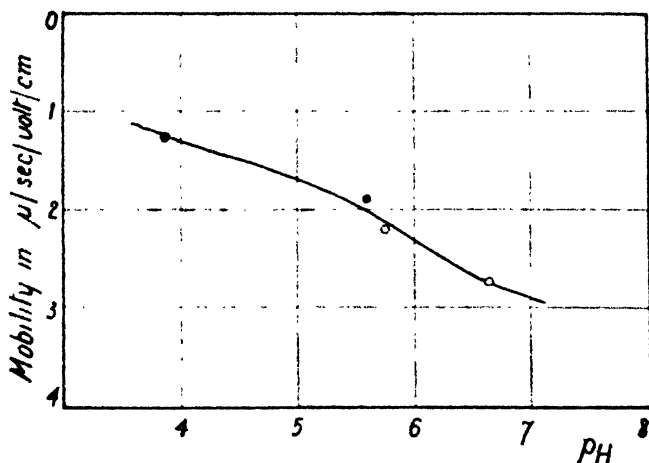


FIG. 7.—Wheat starch in solutions of ionic strength 0.001.

● Acetate buffer.
○ Phosphate buffer.

5. The * Lipids of Flour.—The lipids of flour were extracted with petroleum ether, and acetone was added after partial removal of the petroleum ether. The acetone solution was mixed with water to give a dispersion of lipids, and the solvents were removed by aeration. The results are given in Fig. 4.

* The term "lipids" denotes here all petroleum-ether soluble substances.

6. The Glutens from Flour.—The cataphoretic behaviour of gluten obtained by kneading Manitoba Flour is expressed in Fig. 5. The isoelectric reaction of the gluten is $p_H 5.72 \pm 0.07$ in acetate buffers, and $p_H 6.12 \pm 0.05$ in phosphate buffers, of ionic strength 0.02, and $p_H 6.30 \pm 0.07$ in phosphate buffers of ionic strength 0.001.

The application of the additive rule to these results, in conjunction with those of sections 4 and 5, indicates that the mean value of the surface fraction of natural mixed proteins is 0.9. In the case of English flour (Fig. 6), the surface fraction of proteins also varies about a mean figure of 0.9. The effect of heat denaturation upon the cataphoretic behaviour of gluten from English flour was investigated, the results being given in Fig. 6. The isoelectric point is changed from $p_H 6.44 \pm 0.05$ to $p_H 5.92 \pm 0.05$ by heating to 90° C. for 6 hours, and it is inferred that during the process of baking, basic groups of the protein disappear.

7. Starch.—The cataphoretic behaviour of wheat starch is shown in Fig. 7.

8. Flours.—The mean mobilities of the particles of Manitoba and English flours were measured in acetate buffers of ionic strength 0.001 (see Table II.). If we denote by f_G the fraction of gluten on the surface of the "average" flour particle, then assuming an additive law, we have

TABLE II.

Flour.	p_H .	Mobility.
Manitoba .	3.90	+ 1.20
	4.80	+ 0.60
English .	3.86	+ 0.96
	3.92	+ 0.92

$$\mu_F = f_G \mu_G + (1 - f_G) \mu_S$$

where μ_F , μ_G and μ_S denote the mobilities of particles of flour, of gluten, and of starch respectively. From the results of sections 6 and 7, the fractions of gluten on the surface of particles of Manitoba flour obtained are 0.78 at $p_H 3.90$ and 0.79 at $p_H 4.80$. In the case of English flour, no results were available for the mobility of gluten particles in acetate solutions of ionic strength 0.001. However, it was possible to obtain an approximate value of the mobility of the gluten from English flour in these solutions by combining the results of sections 4, 5 and 6 with the conclusion of section 6 that the surface fraction of mixed proteins in the gluten particle from English flour is approximately 0.9. Thus the mobility of particles of English gluten could be obtained from the mobilities of particles of the natural mixed proteins (section 4) and of the lipoids (section 5). This method gave an approximate value of 0.8 at $p_H 3.9$ for the surface fraction of the particle of English flour covered with gluten.

There is apparently little difference between the surface composition of the particles of English and Manitoba flours, the fraction of the surface covered with gluten being in each case about 0.8.

Summary.

1. A method for the surface analysis of colloidal particles is described.
2. The cataphoretic behaviour of the following colloidal constituents of wheat flours has been studied :—

- (a) Glutenin. The effect of salt concentration on the isoelectric reaction is discussed.
- (b) Gliadin. Alcohol-denaturation is shown to eliminate basic groups, shifting the isoelectric point to the acid side.
- (c) Natural protein mixtures from Manitoba and English flours.
- (d) Lipoids from the two flours.
- (e) Glutens from the two flours. The effect of baking is to shift the isoelectric point to the acid side, showing that basic groups are removed.
- (f) Wheat starch.

3. The distribution of proteins and lipoids over the surface of particles of the flours is discussed. The results indicate that for Manitoba and English flours the fraction of the particle surface covered by gluten is about 0.8.

The author desires to thank Professor E. K. Rideal, F.R.S., for his encouragement and assistance, and the Research Association of British Flour Millers for financial assistance in this work and for permission to publish the results. He is also indebted to Dr. E. A. Fisher for helpful discussions.

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Cambridge.*

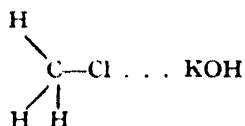
SUBSTITUTION AND INVERSION OF CONFIGURATION.

By E. BERGMANN, M. POLANYI AND A. L. SZABO.

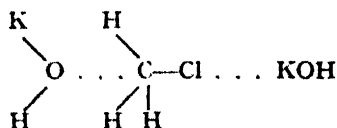
Received 25th February, 1936.

In a previous paper¹ the authors communicated experiments on the racemisation of optically active methyl butyl and methyl propyl iodomethane by iodine ions, and connected their results with the known data on substitution of the analogous chlorides by iodine ions. Before presenting our further experiments² we wish to make clear the previous development leading up to our own work.

Walden inversion was first connected with the spatial mechanism of the substitution, by A. Werner.³ His ideas, which have been further developed by A. Meisenheimer⁴ may be demonstrated for the case of the alkaline hydrolysis of methylchloride. This is supposed to occur in two steps, the first of which is the addition of one molecule of KOH to the methyl chloride



linking the potassium atom to the chlorine atom. The formation of this compound involves a distortion of the carbon tetrahedron reinforcing the positive character of the central carbon atom, and enabling a second molecule of KOH to combine through the oxygen atom with the methyl chloride molecule



¹ *Z. physik. Chem. (B)*, 1933, **20**, 161.

² For a preceding publication of these results see the thesis of one of the authors; A. Szabo, *Diss. Berlin*, 1933.

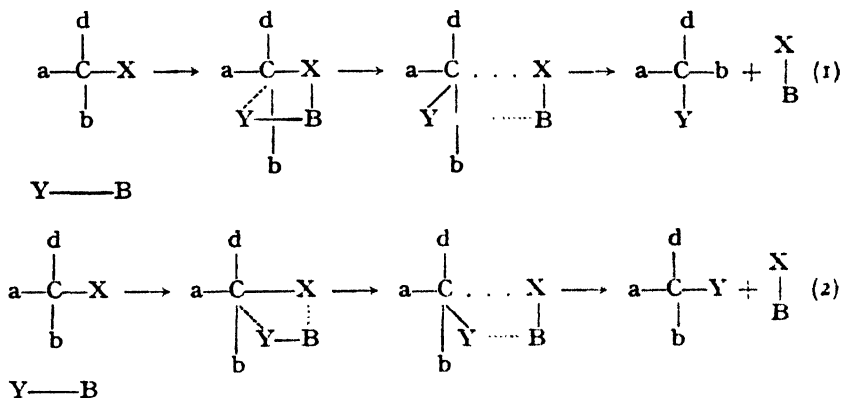
³ *Lehrbuch der Stereochemie*, Jena, 1904, pp. 14 and 15.

⁴ *Liebig's Ann.*, 1927, **456**, 126.

From this complex, methyl alcohol is formed either with the KOH molecule to the left or with that to the right, inversion occurring in the former, not in the latter case.

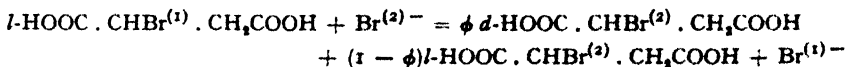
Although the theory of Werner and Meisenheimer is certainly incorrect in detail and does not allow one to predict the course of any particular reaction, it gives an important lead by suggesting a spatially directed mechanism of substitution.

Br. Holmberg^{4a} (writing a year before Meisenheimer's paper appeared) attempted another detailed picture of spatially directed substitution; we present it in the form given by Wagner-Jauregg.⁵ When colliding with a molecule BY, the compound $abdCX$ is supposed to take up the alternative series of arrangements (1) or (2)



The first process leads to inversion of configuration, while in the latter case the original configuration is retained. Whether the former or the latter prevails is supposed to depend on the "reaction distance" $Y-B$. The predictions based on this theory have, as Wagner-Jauregg⁵ remarks, in general not been borne out by experiments.

To the alkali chlorides acting on organic halides Holmberg attributes a large "reaction distance" $Y-B$ between the kation and anion, or alternatively suggests that the anion might act alone with a large "reaction distance" $E-A$, representing the distance between the anion A and its negative charge E . This description of the substitution (which fails to convey any meaning to us), is used by Holmberg to account for the tendency discovered by him for substitution by negative ions to produce inversion of configuration. Holmberg does not claim that substitution by negative ions necessarily leads to inversion of configuration. This is apparent in the following formulation which he gives for his explanation of the racemising effect of halogen ions on halogeno-succinic acids:



where ϕ is the fraction of substitution reactions leading to inversion and $(1 - \phi)$ the fraction reacting *without* configurational change.

Holmberg's general idea, that racemisation of this type is due to atomic interchange reactions, has since been confirmed. The evidence given by Holmberg, however, was questioned by Wagner-Jauregg,⁶ who suggested that the racemisation of bromo-succinic acid and similar compounds is due to enolisation.

The theoretical situation in 1931 seems to be correctly characterised

^{4a} *Ber.*, 1926, **59**, 126.

⁵ Freudenberg's *Stereochemie*, Vienna, 1933, p. 908.

⁶ *Monatshefte der Chemie*, 1929, **53-54**, 791.

by Hueckel.⁷ "Hitherto none of the speculations on the course of a substitution at an asymmetric carbon atom is based on experimental evidence. None of these speculations give a definite lead to experiments to set an aim to further investigation."

In a paper by N. Meer and one of the authors⁸ it was pointed out that, when a substituent of the negative type is exchanged for a negative ion, the driving force of the reaction must lie in the interaction of the negative ion with the carbon atom to which it becomes attached in the course of the reaction; the effect of the positive ion is restricted to a "salt effect." It was further pointed out that the negative ion will necessarily approach the carbon atom from the side opposite to the group to be substituted, since the electrostatic forces of the dipole attacked by the ion will cause this to be a position of minimum energy. In consequence it was claimed that substitution by negative ions is necessarily connected with configurational inversion.

As evidence for the correctness of these views it has been pointed out that substitution by negative ions is accompanied by steric hindrance when voluminous substituents are attached to the carbon atom at which the substitution takes place.

Further strong evidence in favour of the theory of Meer and Polanyi were given by the present authors.^{1,2} The kinetic analysis by Olson and Long³ of the substitution of optically active halogen succinic acids by halide ions offers an even more conclusive proof of this theory. A direct demonstration of its correctness has recently been given by Hughes, Juliusburger, Masterman, Topley and Weiss,¹⁰ who showed that atomic interchange between radioactive iodine ions and optically active alkyl iodides is accompanied by inversion of symmetry.

General Results.

The following two conclusions drawn from the theory of substitution have been tested or partly tested. 1. The racemisation of an optically active halide by the corresponding halogen ion should follow the laws which are known to obtain in substitutions by halogen ions, *i.e.*, the velocity constant should be expressed by the Arrhenius equation containing a temperature independent factor of about 10^{10} . 2. The magnitude of these constants should quantitatively fit into a pattern which includes the analogous substitution reactions (Table I.). In

TABLE I.

Organic Halide.	Inorganic Ion.			
	F ⁻ .	Cl ⁻ .	Br ⁻ .	I ⁻ .
Fluoride	Rac.	Subst.	Subst.	Subst.
Chloride	Subst.	Rac.	Subst.	Subst.
Bromide	Subst.	Subst.	Rac.	Subst.
Iodide	Subst.	Subst.	Subst.	Rac.

any vertical or horizontal column of this pattern the velocity constants should show a monotonous sequence, so that it should be possible to calculate the rates of racemisation by interpolating or extrapolating from

⁷ *Theoretische Grundlagen der organischen Chemie*, Leipzig, 1931, p. 288.

⁸ N. Meer and M. Polanyi, *Z. physik. Chem.*, 1932, 19B, 164.

⁹ *J. Amer. Chem. Soc.*, 1934, 56, 1294.

¹⁰ *J. Chem. Soc.*, 1935, 1525.

the rates of substitution. Monotonous sequence should also be found along the diagonals of the table, and along lines parallel to these.

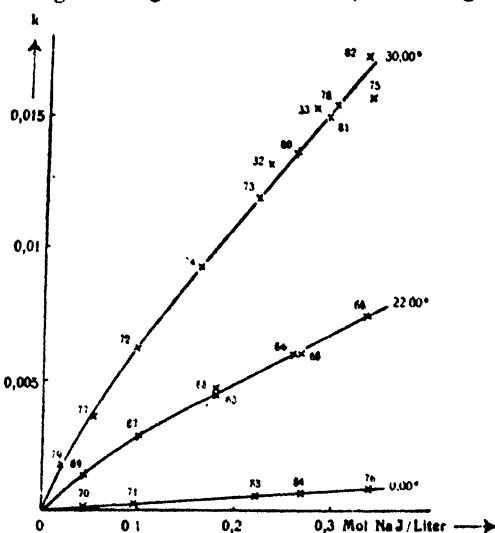


FIG. 1.—Velocity constants of the racemisation of methylpropyl iodomethane by NaI.

The main difficulty in following the sequences set out in the above table for any single compound is that the range of velocities is too wide. In consequence one has to change over from one radical to another and to calculate the missing data by relating the values which could be determined for both cases. In view of the uncertainties involved in the use of compounds where enolisation is possible we chose for our investigation pure secondary alkyl halides, namely, methyl-butyl, methyl-propyl, and methylphenyl halogenomethanes.

The results obtained for the reaction between iodomethane and iodine ions are summarised in Figs. 1 and 2. The curves represent the bi-molecular velocity constants

$$k_2 = \frac{1}{2 \cdot c \cdot t} \cdot \log \frac{\alpha_0}{\alpha_t}$$

where α is the observed rotation, t the time in minutes and c the concentration of the inorganic halide.

The factor $\frac{1}{2}$ is due to the substitution of each molecule wiping out the optical activity of two active molecules.

The Arrhenius equations representing k_2 change slightly with concentration; for 0.1 N concentration of I⁻ we found

$$\log k_2 = \log 10^{10.7} - \frac{17000}{2.3 RT}$$

for methylbutyl iodo-methane, and

$$\log k_2 = \log 10^{11.0} - \frac{17400}{2.3 RT}$$

for methylpropyl iodo-methane.

While the activation energy does not show a definite trend with concentration, the values for the collision number decrease with increas-

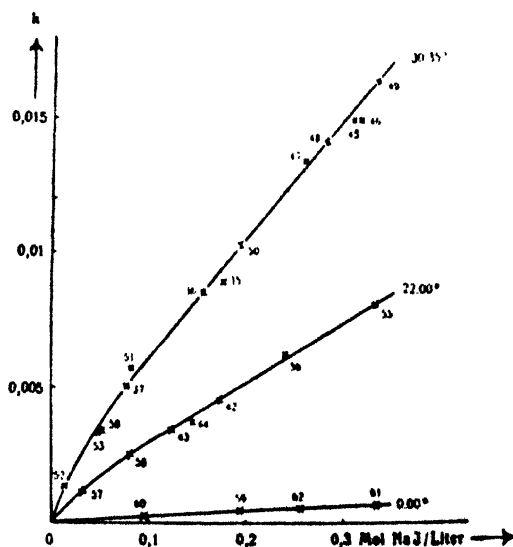


FIG. 2.—Velocity constants of the racemisation of methylbutyl iodomethane by NaI.

ing concentration (as shown by the curvature) owing to the decrease of activity of the iodine ions with increasing concentration. The decrease is from $10^{10.9}$ to $10^{10.6}$ for methylbutyl- and from $10^{11.1}$ to $10^{10.9}$ for methylpropyl iodomethane. These values are in satisfactory agreement with the collision numbers found in other reactions involving substitutions by negative ions.¹¹

Our further results are listed in Table II. From the data for the first three reactions, in conjunction with the value of the velocity constant of

TABLE II.—SUBSTITUTION REACTIONS IN ANHYDROUS ACETONE.

	Temp. °C.	k_2	$c_{\text{inorg.}}$
1. Methylbutyl-bromomethane + NaJ	30	1.3×10^{-3}	0.3037
2. Methylbutyl-chloromethane + NaJ	50	7.4×10^{-3}	0.3005
3. Methylpropyl-fluoromethane + NaJ	50	1.2×10^{-3}	0.3042
4. Methylphenyl-chloromethane + LiCl	120	6.0×10^{-3}	0.3416
5. Methylphenyl-chloromethane + NaJ	50	5.7×10^{-3}	0.036
	50	1.0×10^{-3}	0.193 ¹²

the corresponding racemisation, a sequence is obtained which corresponds to the last column of Table I. This sequence is presented for the common temperature of 50° C. in Table III. In computing these data, a temperature coefficient of 2.4 per 10° (as observed for reaction 2) was assumed for reaction 3. We also made the obviously justifiable assumption, that the value for methylbutyl fluoromethane is the same as that measured for methylpropyl fluoromethane.

The reaction velocities form a monotonous series, thus confirming the expectation expressed above. There is an increase in the sequence $F \rightarrow Cl \rightarrow Br \rightarrow I$, as usually

found in analogous cases. An extrapolation based on the first three figures of the sequence yields a value for the racemisation of the iodide, which is in satisfactory agreement with the measured one.

A second shorter sequence included in the data given above is that of the reactions of phenylmethyl chloromethane with chloride and iodide ions respectively. The considerable increase of reaction rate on passing from Cl^- ($k_2 = 5.7 \times 10^{-3}$) to I^- ($k_2 = 1.0 \times 10^{-3}$) is analogous to the increase referred to above in the series of organic halides.

We have attempted and failed to determine the racemisation velocity of methylbutyl chloromethane by chloride ions; the optically active compound showed no decrease in rotation when exposed to the influence of 0.036 mol. LiCl at 50° C. for fourteen days. This result can be accounted for by the following rough calculation. Assuming that the ratio of velocities for the two pairs of reactions (a) phenylmethyl-chloromethane + I^- (1.0×10^{-3}) and phenylmethyl chloromethane + Cl^- (5.7×10^{-3}), and (b) methylbutyl chloromethane + I^- (1.2×10^{-3})

TABLE III.—REACTION OF METHYLBUTYL HALOGENOMETHANE WITH SODIUM IODIDE (0.3 MOL./LITRE) IN ANHYDROUS ACETONE AT 50° C.

	k_2
Fluoromethane	1.3×10^{-7}
Chloromethane	1.2×10^{-6}
Bromomethane	7.4×10^{-3}
Iodomethane	1.4×10^{-1}

¹¹ Moelwyn-Hughes, *Chem. Rev.*, 1932, 10, 242; *Kinetics of Reactions in Solution*, Oxford, 1933.

¹² These figures represent preliminary measurements and are not very accurate.

and methylbutyl chloromethane + Cl^- are the same, the latter reaction would have (at 50°) a velocity constant of $k_2 = 6.8 \times 10^{-7}$, which at the concentration of 0.036 mol./litre LiCl , as used above, would only lead to a measurable decrease of rotation in about one year.

Olson and Long⁹ have found the following data for the four reactions of chlorosuccinic and bromosuccinic acid with Cl^- and Br^- (50° , aqueous solution, 2 *N*-hydrogen ions).

	Chloride ions.	Bromide ions.
Chlorosuccinic acid	4.8×10^{-8}	2.0×10^{-8}
Bromosuccinic acid	1.0×10^{-8}	7.0×10^{-8}

The sequence of these figures is analogous to that given above.

Experimental Part.

Racemisation Experiments.

For the racemisations the experimental procedure was exactly as in our first paper, *i.e.*, to fill up weighed amounts of organic and inorganic halides with anhydrous acetone to 10 c.c. These solutions were filled into water jacketed polarimeter tubes, which were kept in thermostats and were only removed from there for the short times during which readings were being taken.

Substitution Reactions.

The substitution reactions were carried through according to the method of Conant and co-workers.¹³ Thus the reaction between phenyl methyl chloromethane and sodium iodide was followed by titrating the amount of iodide ions with potassium iodate. By this method both iodide ions and free iodine are titrated; therefore, the iodine set free by decomposition of the phenyl methyl iodomethane formed was determined separately and accounted for by subtracting an equivalent amount from the potassium iodate used.

The isolation of the products of this reaction was carried through by distillation *in vacuo*. The reaction mixture was filtered, evaporated, the residue dissolved in ether, washed with potash solution and water, dried and distilled. The first fraction (b.p. $33^\circ/14$ mm.) consisted of styrene and ethylbenzene. The styrene always prevailed (normally 70 per cent.), which may be accounted for according to the considerations of Meinert¹⁴ and F. O. Rice.¹⁵ The residue was again dissolved in ether, treated with sodium thiosulphate solution and distilled at 0.1 mm. pressure. The first fraction (b.p. $40-45^\circ$) always showed a dark brown colour which, even after repeated distillations, reappeared. The analysis showed an iodine content of 29.2 per cent. (calculated for $\text{C}_6\text{H}_5\text{I}$, 54.8 per cent.). The next fraction (b.p. $80-110^\circ$) showed after distillation the b.p. $80-84^\circ$ at 0.25 mm. and was according to that boiling-point and the analysis (Found: C, 90.4; H, 9.0. Calculated for $\text{C}_{12}\text{H}_{18}$; C, 91.4; H, 8.6) dimethyl diphenyl ethane in its liquid racemic form.¹⁶

This experiment has also been carried out using optically active phenyl methyl chloromethane. But since the racemisation of phenylmethyl iodomethane by iodide ions probably occurs some 10,000 times faster than the substitution of the corresponding chloride by iodide ions (compare Table III.), one cannot expect to obtain optically active phenyl methyl iodomethane. Neither this compound nor the dimethyl diphenyl ethane showed a marked optical activity.

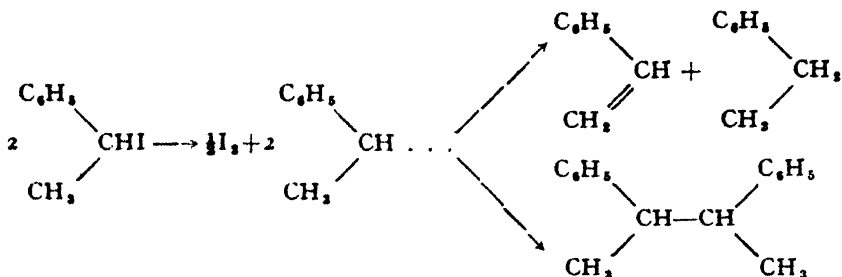
¹³ *J. Amer. Chem. Soc.*, 1924, **46**, 233; 1925, **47**, 476, 587.

¹⁴ *Ibid.*, 1933, **55**, 979.

¹⁵ *Ibid.*, 1931, **53**, 1959.

¹⁶ Compare Ott; *Ber.*, 1928, **61**, 2124.

The decomposition of phenylmethyl iodomethane described above is analogous to that of triphenyl iodomethane, which splits spontaneously into iodine and triphenyl methyl radicals,¹⁷ the difference being that the free phenyl methyl radical is unstable and partly disproportionates into styrene and ethylbenzene, and partly dimerises into sym. dimethyl diphenyl ethane



Preparation of Materials.

The preparation of phenylmethyl chloromethane and anhydrous acetone have been described in our first paper. Methylpropyl fluoromethane is prepared in the following way: 14 gms. of silver fluoride are carefully mixed with 42 g. of quartz sand in a mortar and introduced into a reaction flask, stoppered with a rubber stopper with three holes. A dropping funnel is placed into one of the holes, while into the two others glass tubes are fitted for drawing off the fluoromethane formed and introducing nitrogen into the flask. While a slow stream of nitrogen (5-6 bubbles per min.) passes through the apparatus, 20 g. of methylpropyl iodomethane are introduced into the reaction vessel. The reaction occurs immediately, the solid phase turning yellow. The current of nitrogen takes the fluoromethane into a receiver combined from a U-shaped tube heated to 60° C. and a condenser connected with a suction flask cooled to -30°. The U-tube serves for removing the unchanged iodomethane from the reaction products; the fluoromethane is condensed in the receiver (closed by a calcium chloride tube) and is purified by repeated distillation. B.p. 48-50°/756 mm. (Found: C, 67.0; H, 12.3, calculated for C₃H₇F: C, 66.7; H, 12.2).

Methylbutyl fluoromethane, prepared in an analogous manner, has the b.p. 60-72°/759 mm.

Methylbutyl chloromethane was prepared according to Levene and Mikeska¹⁸; for the preparation of the corresponding bromo derivative we used exactly the same method as was described by J. H. Green.¹⁹

In Tables I. and II. the results of four experiments are given in full; Table III. gives a complete presentation of the graphically averaged constants of all experiments. The notations used are:—

α measured rotation.

$$k_1 \text{ first order constant } k_1 = \frac{\log \frac{\alpha_0}{\alpha_t}}{t}$$

k_2 reaction constant for the substitution underlying the racemisation,

$$k_2 = \frac{1}{2} \cdot \frac{k_1}{C_{\text{inorg. halide}}}$$

t time in minutes.

¹⁷ Gomberg, *Ber.*, 1900, **33**, 3158.

¹⁸ *J. Biol. Chemistry*, 1927, **75**, 587.

¹⁹ *J. Amer. Chem. Soc.*, 1934, **56**, 1167.

TABLE I.

	<i>t</i> .		<i>k</i> ₁ .	<i>k</i> ₂ .
Experiment 45.				
0.5442 g. (0.257 mol./litre)	0	— 0.70	—	
methyl butyl iodomethane	10	50	0.0146	
and 0.4630 g. (0.309 mol./litre) sodium iodide. <i>T</i> = 303.40° K.	20	36	145	
	32	24	145	
	45	15	148	
	60	09	148	
		Average :	0.0146	0.0239
Experiment 57.				
0.4288 g. (0.202 mol./litre)	0	— 0.73	—	
methyl butyl iodomethane	20	685	(0.00138)	
and 0.0478 g. (0.032 mol./litre) sodium iodide. <i>T</i> = 295.05° K.	50	645	107	
	120	54	108	
	200	45	105	
	290	34	114	
	400	25	116	
	540	175	114	
		Average :	0.00115	0.0180
Experiment 74.				
0.434 g. (0.219 mol./litre)	0	— 0.82	—	
methyl propyl iodomethane	10	665	0.00910	
and 0.2398 g. (0.160 mol./litre) sodium iodide. <i>T</i> = 303.30° K.	23	50	934	
	30	42	908	
	40	35	924	
	55	25	938	
	70	19	907	
	100	10	914	
	130	055	903	
		Average :	0.00911	0.0285

TABLE II.

	<i>t</i> .	<i>a</i> - <i>x</i> .	<i>b</i> - <i>x</i> .	<i>k</i> ₂ .
Experiment I.				
Methyl butyl bromomethane	1282	0.2462	0.0946	1.36 . 10 ⁻
(0.1521 mol./litre) sodium	1522	2392	876	1.36
iodide (0.3037 mol./litre)	1815	2371	855	1.19
<i>T</i> = 303° K.	2718	2134	618	1.33
			Average :	1.31 . 10 ⁻

TABLE III.

No. of Exper.	Reaction.	Temp. °K.	Concentration in Moles/Litre of		k_1 .	k_2
			Organic Halide.	Inorganic Halide.		
45	sec. $C_6H_{11}I + NaI$	303.40	0.257	0.309	0.0146	0.0239
46	" "	303.30	.210	.302	.0139	.0230
47	" "	"	.211	.260	.0133	.0261
48	" "	"	.210	.285	.0140	.0247
49	" "	"	.285	.336	.0164	.0244
50	" "	"	.222	.193	.0105	.0272
51	" "	"	.230	.081	.0057	.0352
52	" "	"	.230	.012	.00134	.0558
53	" "	"	.194	.047	.00342	.0364
54	" "	"	.205	.122	.00770	.0316
55	" "	295.10	.242	.333	.00798	.0120
56	" "	295.05	.205	.239	.00612	.0128
57	" "	"	.202	.032	.00115	.0180
58	" "	"	.193	.079	.00246	.0156
59	" "	273.0	.187	.193	.00051	.00132
60	" "	"	.184	.094	.00024	.00128
61	" "	"	.194	.333	.000725	.00109
62	" "	"	.184	.257	.00057	.00111
63	.. $C_6H_{11}I + NaI$	295.00	.15	.179	.0045	.0126
64	" "	"	.205	.258	.00575	.0111
65	" "	"	.15	.266	.00590	.0111
66	" "	"	.190	.333	.00737	.0110
67	" "	"	.160	.100	.00273	.0136
68	" "	"	.190	.170	.00472	.0134
69	" "	"	.145	.042	.00146	.0174
70	" "	273.0	.205	.042	.000123	.00146
71	" "	"	.137	.095	.000246	.00129
72	" "	303.00	.206	.095	.00623	.0328
73	" "	"	.218	.221	.0121	.0274
74	" "	303.30	.219	.100	.00911	.0285
75	" "	303.00	.189	.339	.0157	.0231
76	" "	273.0	solution of Ex. 75		.00080	.00118
77	" "	303.00	.209	.051	.00349	.0342
78	" "	"	.208	.300	.0152	.0253
79	" "	"	.217	.019	.00163	.0429
80	" "	"	.228	.260	.0135	.0260
81	" "	"	.217	.291	.0149	.0256
82	" "	"	.270	.339	.0175	.0258
83	" "	273.0	.214	.218	.00049	.0011
84	" "	"	.223	.268	.000564	.00105
86	.. $C_6H_5Cl + LiCl$	323	.205	.031	no decrease in rotation	
87	.. $C_6H_5(CH_2)CHCl + LiCl$	"	.305	.036	$4.1 \cdot 10^{-5}$	$5.7 \cdot 10^{-5}$
I.	.. $C_6H_5Br + NaI$	303	.152	.304	—	$1.31 \cdot 10^{-5}$
II.	" "	323	.149	.300	—	0.0074
III.	.. $C_6H_5Cl + NaI$	"	.150	.304	—	$1.2 \cdot 10^{-5}$
IV.	.. $C_6H_5(CH_2)CHCl + NaI$	"	.093	.193	—	0.0010

Summary.

A kinetic study of the racemisation of methylpropyl iodomethane and of methylbutyl iodomethane by iodine ions in connection with studies of related substitution reactions has brought additional evidence for the theory of substitution of organic halogen compounds by halogen ions.

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AN ELECTRON-DIFFRACTION STUDY OF THE STRUCTURE OF ELECTRO - DEPOSITED METALS.

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1. Introduction.

A more or less pronounced tendency for the crystals to orientate in accordance with a position of maximum mechanical stability can generally be observed when a crystalline film is formed by the deposition of crystals upon a substrate. For example, in the case of colloidal solution of graphite, the crystals of which are known to be exceedingly thin in the *c* axial direction but of relatively large cleavage plane dimensions, the particles settle out in such a manner that this plane is parallel to the substrate. On the other hand, when the crystals are formed on the substrate as, for example, by the condensation of vapour or by chemical attack, the substrate may either serve as a virtually inert supporting medium in contact with which the most readily formed external plane of the crystal is developed, or the substrate crystals may themselves govern the orientation of the deposited crystals by determining the type of face first developed on condensation. Many examples are known of the first case which is, in effect, virtually the parallel to that in which already formed crystals take up an orientation imposed by considerations of mechanical stability. Thus, Kirchner¹ found that cadmium iodide formed by the condensation of the vapour on a celluloid film was orientated with the (001) planes parallel to the support, and even more striking was Jenkins'² observation that the crystalline oxide scums on molten lead, tin, zinc and bismuth displayed similar orientation effects. Examples of the substrate playing the much more active rôle of causing the deposit crystals to adopt the orientation of those of the substrate are less frequent, but well-authenticated cases of crystals being constrained by the substrate into taking up unusual modes of orientation are known. Thomson,³ for example, showed that silver electro-deposited on an etched copper cube face rigidly followed the orientation of the copper ;

¹ Kirchner, *Ergeb. exakt. Naturw.*, 1932, 11, 64.

² Jenkins, *Proc. Physic. Soc.*, 1935, 47, 109.

³ Thomson, *Proc. Roy. Soc.*, 1931, A133, 1.

and Finch, Quarrell and Wilman⁴ found that crystals formed by the cathodic sputtering of gold under conditions favourable to the production of a random film exhibited (111) orientation when deposited on platinum of similar orientation, but were randomly disposed when grown on a glass surface. Even more intense are substrate effects such as those giving rise to the phenomenon of pseudomorphism⁵ and the dissolution of crystalline metal films in the polish layer on metals.⁶

Jenkins⁷ and Finch, Quarrell and Wilman⁴ have drawn attention to the fact that a film of orientated graphite crystals adheres much more strongly to a substrate than does a similar but unorientated layer, and Finch, Quarrell and Roebuck⁶ remarked that certain metal films formed by condensation of the vapour are firmly held only by a polished but not by a crystalline metal substrate. On the other hand, as far as we are aware, the effect on the adhesion of a deposit, the crystal orientation of which has been determined by that of the substrate, has not been examined.

Some of the problems hinted at in these introductory remarks have already been the subject of study by X-rays.⁸ The limitations of this method, however, when applied to such cases of surface phenomena are obvious. Thus, our interest centres in the main about the region of contact between substrate and deposit; and a probable change between abnormality in, for example, the orientation in the first deposit layers and a more usual type of orientation possibly reverted to with growing film thickness might well escape detection by X-rays, particularly if the change were at all rapid. On the other hand, the subject is one which appears eminently suitable for study by the method of electron diffraction.

The object of the experiments described below was to study by electron diffraction surface orientation effects and their associated phenomena as exhibited by electro-deposited metal films, not only at grazing incidence but also by transmission. In addition to preparing specimens mounted on massive substrates and therefore only suitable for examination at grazing incidence, we have been able to devise methods for producing robust metal films, by either electrodeposition or chemical displacement, which were sufficiently thin for transmission purposes and consisted, as desired, of the deposit either alone or together with the substrate. We have found, *inter alia*, that whilst in the case of chemical deposition the change from substrate to deposit is a gradual one of alloying, in electrodeposition the composition change is abrupt, though the substrate orientation nearly always profoundly affects that of the initial deposit layers. In certain cases, characterised by inability of the substrate to impose a definite orientation on the crystals in the deposit, poor adhesion was observed.

2. Preparation of Reflection Specimens.

The metal to be examined was electrodeposited either on to a metal layer previously deposited on a suitable metal disc, such as copper, or directly on to the disc. After plating, the specimen was washed with

⁴ Finch, Quarrell and Wilman, *Trans. Faraday Soc.*, 1935, 31, 1051.

⁵ Finch and Quarrell, *Proc. Roy. Soc.*, 1933, A141, 398.

⁶ Finch, Quarrell and Roebuck, *ibid.*, 1934, A145, 676.

⁷ Jenkins, *Phil. Mag.*, 1934, 17, 457.

⁸ Frolich, etc., *Trans. Am. Electrochem. Soc.*, 1925, 49, 369; Wood, *Proc. Phys. Soc.*, 1931, 43, 138.

distilled water and rapidly dried by evacuation in the electron-diffraction camera. The deposition conditions are given in Table I.

TABLE I.

Metal.	Bath Composition (g./l.).	Current Density A./dm ² .	Bath Temperature °C.
Cu	Cu(C ₂ H ₃ O ₂) ₂ · H ₂ O, 25 g.; Na ₂ SO ₄ · H ₂ O, 50 g.; KCN, 35 g.; Na ₂ CO ₃ , 10 g.	0·3	20
Au	AuCl ₃ · NaCl, 2 g.; KCN, 15 g.	0·1	50
Ag	AgCN, 36 g.; KCN, 52 g.; K ₂ CO ₃ , 38 g.	1·0	20
Fe	FeSO ₄ · (NH ₄) ₂ SO ₄ · 6H ₂ O, 350 g.; H ₂ SO ₄ , 2·5 g.	1·0	20
Co	CoSO ₄ · (NH ₄) ₂ SO ₄ · 6H ₂ O, 175 g.; NaCl, 17 g.; H ₃ BO ₃ , 50 g.	1·0	20
Ni	NiSO ₄ · 7H ₂ O, 50 g.; Na ₂ C ₄ H ₇ O ₇ , 20 g.	0·2	50
Sn	SnCl ₂ · 2H ₂ O, 11·5 g.; KOH, 62 g.; KCN, 13·5 g.	0·5	50
As	As ₂ O ₃ , 50 g.; KCN, 50 g.; Na ₄ P ₂ O ₇ · H ₂ O, 20 g.	7·0	80
Sb (amorphous)	SbCl ₃ , 200 g.; HCl, 300 c.c.	8·0	80
Sb (crystalline)	Schlippe's salt, 50 g.; Na ₂ CO ₃ , 10 g.	0·5	70
Bi	Bi ₂ O ₃ · CO ₂ · H ₂ O, 47 g.; H ₂ ClO ₄ , 19 g.	0·5	50
Cr	CrO ₃ , 250 g.; H ₂ SO ₄ , 2·5 g.	13·5	20
α-Brass	Cu(C ₂ H ₃ O ₂) ₂ · H ₂ O, 12·5 g.; KCN, 23 g.; Zn(C ₂ H ₃ O ₂) ₂ · H ₂ O, 16·2 g.; Na ₂ CO ₃ , 10 g.; Na ₂ SO ₄ · H ₂ O, 50 g.	0·5	20
Pt	H ₂ PtCl ₆ · 6H ₂ O, 13·3 g.; (NH ₄) ₂ HPO ₄ , 45 g.; Na ₂ HPO ₄ · 12H ₂ O, 240 g.	0·4	70
Cd (as basis metal)	CdO, 32 g.; NaCN, 75 g.	1·1·5	20
Zn (as basis metal)	ZnSO ₄ · 7H ₂ O, 240 g.; NH ₄ Cl, 15 g.; Al ₂ (SO ₄) ₃ · 18H ₂ O, 30 g.	5·10	20

3. Orientation in the Absence of Substrate Effects.

Preliminary experiments were carried out with the main object of determining the normal type of crystal orientation assumed in the various metal films formed under the electrodeposition conditions outlined in Table I. Amorphous or polished metal substrates were used in order to preclude as far as possible any specific orientating influence such as might possibly be exerted by the crystalline substrate. The results obtained are summarised in Table II., and typical patterns illustrating some of the more striking orientation effects are produced in Figs. 1, 2 and 3. As previously,⁴ we continue to define the direction of orientation in terms of the indices of planes parallel to the substrate surface or specimen film.

In the case of zinc, evidence was obtained of the layers first deposited going into solution in the polished copper surface. Thus, in order to obtain a zinc layer sufficiently thick to afford a pattern recognisable as characteristic of a crystalline structure, it was necessary to deposit from the cyanide bath at 0·08 A./dm.² and 20° C. during at least 3 minutes on to a polished copper substrate, whilst 30 seconds sufficed with a crystalline copper substrate, other conditions being the same. In view of the results obtained by Finch, Quarrell and Roebuck⁵ in their study of the surface action of the Beilby layer it is quite probable that a similar preliminary solution of deposit in substrate occurred to a greater or lesser extent in the majority of the cases of deposition on polished substrates set forth in Table II. The fact that even the thin deposits on arsenic were for the most part well orientated supports this view and suggests further that the electrodeposited arsenic substrate was not in fact amorphous but consisted rather of exceedingly small crystals.

The types of orientation set forth in Table II. and exhibited by thin

layers on arsenic and by all the thick deposits may be taken as normal and representative of the plating conditions outlined in Table I. In some cases, for example, α -brass and gold, where in the same specimen some crystals exhibited one and others another direction of orientation, the second type of orientation has been traced to bath concentration changes occurring during deposition. Thus, a fresh gold bath always led to a mixture of (111) and (100) orientated crystals, whilst a partially used bath in which the gold contents had been enriched from the anode yielded crystals of (111) (Fig. 2) orientation alone.

TABLE II.—SUBSTRATE ORIENTATION EFFECTS ON AMORPHOUS SURFACES.

Substrate.	Substrate Structure.	Deposit.	Orientation in Thin Deposit.	Orientation in Thick Deposit.
Cu, polished	Amorphous	Cu	Random	(110)
		Au	Random	(111) (Fig. 2)
		Ni	Random	(110)
		Fe	(111)	(111) (Fig. 1)
		α -Brass	Random	(111) and (311)
		Pt	Random	(111)
		Sn	Random	(231)
		Bi	Random (Fig. 3)	No definite pattern
Ni, polished	Amorphous	Zn	Random	No definite pattern
		Ni	Random	(110)
Au, polished	Amorphous	Au	Random	(111)
		Au	Random	(111)
As, electro-deposited	{ Amorphous (?), or very small crystals	Au	(100)	(111) and (100)
		Cu weak	(110)	(110)
		Ni	(110)	(110)
		Fe	(111)	(111) (Fig. 1)
		-Brass	(111)	(111) and (311)

4. Substrate Orientation Effects.

In these experiments a basis metal was electrodeposited on to a polished copper disc either in the form of a thin layer exhibiting random crystal array, or to a thickness such that it showed well the normal type of orientation as set forth in Table II., and the specimen metal was in turn deposited on this basis as substrate, the plating conditions being as given in Table I.

When the substrate consisted of fairly large (50-100 Å) crystals in random array, it was found that thin films of iron on copper and of gold or copper on nickel were unorientated, but displayed their normal characteristic orientations with sufficient thickening of the deposits. Thus, thick iron, gold and copper exhibited (111), (111) and (110) orientations respectively. These results suggested a strong substrate orientating influence on the first deposit layers, because otherwise we would have expected to find similar orientations in both thick and thin deposits. This view was strikingly confirmed by results obtained with deposits on electrodeposited substrates the crystals of which were well orientated. The results are set forth in Table III. and representative patterns illustrating some of the more unusual modes of orientation observed and due to substrate effect are reproduced in Figs. 4, 5 and 6.

The outstanding feature of these results is that the crystal orientations of the thin deposits were abnormal except in those few cases where the substrate orientation followed that of the normal type as taken up by the deposit under the conditions outlined in Tables I. and II., or when either copper or nickel were deposited on iron of normal orientation. Further,

the crystal orientation of a thin face-centred cubic metal layer formed on a substrate of similar structure, but of an orientation not normally assumed by the deposited metal, followed that of the substrate, though sometimes some differently orientated crystals were also formed, as in the case of copper (Fig. 6) and nickel on gold in (111) and copper on platinum, likewise in (111) orientation. With increasing thickness of the deposits the orientation in general tended to become less pronounced, and in the cases of nickel and copper on gold in (111) orientation, where the progressive changes could readily be followed, it was observed that this loss in orientation went so

TABLE III.—SUBSTRATE ORIENTATION EFFECTS OF THICK ELECTRODEPOSITS.

Electro-deposited Substrate.	Substrate Crystal Orientation.	Deposit.	Orientation in Thin Deposit.	Orientation in Thick Deposit.
Cu	(110)	Au	(110)*	(111)
		Ni	(110)	(110)
		α -Brass	(110)*	(111) and (113)
		Fe	(100)*	(111)
		Bi	Random*	?
Ni	(110)	Cu	(110)	(110)
		Au	(110)*	(111)
		Fe	(100)* (Fig. 4)	(111)
		Bi	Random*	?
Au	(110)†	Fe	(100)*	(111)
		Cu	(111)* and (100)* (Fig. 6)	(110)
Au	(111)	Ni	(111)* and (100)*	(110)
		Ag	(111)	
		Pt	(111)	(111)
		Fe	(110)* (Fig. 5)	(111)
		Sn	(110)*	(231)
Cu	(111) and (100)‡	Fe	(110)*	(111)
		Sn	(110)*	(231)
Ni	(111) and (100)§	Fe	(110)*	(111)
		Sn	Random*	(231)
		Cu	(110)	(110)
Fe	(111)	Ni	(110)	(110)
		Bi	Random*	?
Pt	(111)	Cu	(111)* and (100)*	(110)
Sn	(231)	Ni	Random*	(110)

* Unusual types of orientations for the electrodeposition conditions used are asterisked.

† Gold in (110) orientation was obtained by deposition on a (110) nickel substrate

‡ Obtained by depositing a thin layer of copper on a (111) gold substrate.

§ Obtained by depositing a thin layer of nickel on a (111) gold substrate.

|| No pattern could be obtained without interfering with and destroying the surface structure by scratching, etc.

far that the patterns became almost characteristic of a random crystal array. With still further thickening, however, crystal orientation once more became pronounced but was now of the normal type. Estimates based on the deposition conditions showed that the effect of the substrate on the crystal orientation in the deposit could still be detected up to a thickness which depended upon the nature of the metal, but was generally of the order of 1,000 Å., and that the normal type of orientation did not as a rule appear strongly until the deposit had become considerably thicker. The persistence of the substrate influence was most marked with nickel and was somewhat affected by the nature of the substrate, being greatest in the case of gold and decreasing with tin, α -brass and copper. Even on

gold, however, the substrate effect was completely lost when the nickel deposit thickness was of the order of 2,000 Å.

No substrate orientating influence could be detected with copper or nickel on iron; thus at a thickness estimated at only 50 Å. the normal (110) orientation appeared in both cases.

Unlike the face-centred cubic deposits on face-centred cubic substrates, the body-centred cubic metal, iron, did not follow the substrate orientation, but exhibited nevertheless a strong substrate influence in that the crystal orientation in thin layers was abnormal; in general this was such that the atom population density in the orientation plane of the deposit crystals approached to that of the substrate. This was also the case with tin on gold or copper.

We have examined the adhesion of the deposits enumerated in Table III. by comparing their resistance to abrasion by rubbing between dry fingers. All showed by this rough test good powers of adhesion with the exception of nickel on tin, and bismuth on iron, nickel or copper, all of which rubbed off easily. Thus it would seem that ability to orientate, even in the thin initial layers of an electro-deposit, is of advantage in securing good adhesion.

5. The Preparation of Transmission Specimens.

As in the case of the experiments outlined above, the electron diffraction examination of the orientating effects of crystalline substrates have hitherto always been carried out with the beam at grazing incidence on specimens mounted on massive substrates. Certain disadvantages are inherent in this method. Thus there is some degree of uncertainty as to the effective camera length, and the error involved might well tend to obscure any lattice distortion effect produced by the substrate. A further inaccuracy is liable to be introduced by the small height to which the crystals project over the shadow-throwing surface; for it is now a matter of experience that, compared with transmission, "reflection" patterns are often inferior from the point of view of ring sharpness, and in many cases the difference in definition is largely to be ascribed to the relaxation of the Laue diffraction condition corresponding to the direction normal to grazed specimen surface. It was chiefly for these reasons that in continuing this study of substrate effects we turned to the use of transmission specimens.

Two methods for preparing this type of specimen by electro-deposition have been developed and previously described,⁴ but have since been considerably improved. In the one, commercial metal leaf floating on the plating bath served as cathode under the conditions outlined in Table I. and was removed from the resulting deposit by submersion in a suitable etching bath. The second method, of more general utility, led to the production of robust transmission specimens which were remarkably uniform in thickness and yielded good diffraction patterns throughout their whole area. In general, the procedure consisted in plating a polished stainless steel disc with a thick layer of some suitable "basis" metal under the conditions outline in Table I. After washing, the disc was further plated with the metal required for examination. The composite basis and specimen metal film was then stripped off the disc and immersed in a reagent to dissolve away the basis metal whilst leaving the specimen metal intact.

In the case of iron, tin, bismuth or arsenic it was found necessary first to plate the steel disc with an exceedingly thin layer of copper or nickel before forming the basis metal film. In this manner iron or tin basis films were deposited on coppered, and bismuth or arsenic on either coppered or nickeled polished stainless steel. The conditions for the electrodeposition of the specimen layer on the basis metal are set forth in sufficient detail in a previous communication⁴ and in the further particulars enumerated above in Table I.

After washing to remove the etching reagent, the specimen was picked up on a fine-meshed nickel gauze and transferred whilst still moist to the

camera and rapidly dried by evacuation. The time of deposition varied with the nature of the metal and current density between a few seconds and about 1 minute. The strength of the specimen film depended largely on the bath temperature and current density and also, though to a lesser extent, on the nature and texture of the basis metal layer. Owing to the low current densities employed, the crystal size increased with, and was determined in the main by, the time of deposition. Composite transmission specimens consisting of two electrodeposited metal layers were also obtained by this method, the second metal being either deposited on the first thin specimen layer prior to stripping, or plated on to a floating and previously suitably thinned leaf acting as cathode.

The preparation of transmission specimens by chemical displacement generally involved the prior formation by electrodeposition and isolation of a thin film of the displacing metal, which was then floated on a suitable salt solution of the metal to be displaced. In some cases a relatively thick film was used, and the excess of metal remaining after partial exchange was removed by the appropriate etching reagent.

6. Orientation in Composite Transmission Films.

In these experiments the specimens consisted of a metal electrodeposited on a commercial leaf which had previously been suitably thinned for transmission purposes. The results are incorporated in Table IV. and illustrated by the patterns, Figs. 7, 8 and 9, which show that the substrates in most cases consisted of more or less well-developed single crystals.

TABLE IV.—SUBSTRATE ORIENTATION EFFECTS ON ELECTRO-DEPOSITS OF SUPERIMPOSED TRANSMISSION SPECIMENS.

Substrate (Commercial Leaf).	Substrate Crystal Orientation.	Deposit.	Orientation in Deposit.	
			First Direction.	Second Direction.
Pt	(110)	Cu	(110) (Fig. 7)	(110) _{Pt} parallel to (110) _{Cu}
		Ni	(110) (Fig. 8)	(110) _{Pt} parallel to (110) _{Ni}
		Co	(110)	(110) _{Pt} parallel to (110) _{Co}
Pd	(100)	Cu	(100)	(100) _{Pd} parallel to (100) _{Cu}
		Fe	(100)	(110) _{Pd} parallel to (100) _{Fe}
Au	(100)	Fe	(100) (Fig. 9)	(110) _{Au} parallel to (100) _{Fe}
		Co	(100)	(100) _{Au} parallel to (100) _{Co}
		Ni	(100)	(110) _{Au} parallel to (100) _{Ni}

These results show that the deposit crystals, like those of the substrate, always exhibited two directions of orientation, at least one of which was common to both substrate and deposit, and the patterns, Figs. 7, 8 and 9, afford convincing evidence of the remarkable degree of faithfulness with which the substrate crystal orientation is followed in these thin films by the deposit. In Figs. 7 and 8, for example, the arcs due to copper and

nickel respectively are virtually exact replicas of the corresponding platinum diffractions, even to the reproduction of minute dots due to larger crystals.

The manner in which the body-centred cubic structure, iron, orientates on a face-centred cubic metal, such as palladium or gold, is of particular interest in that it differs from that encountered in the case of superimposed face-centred cubic structures. Although substrate and deposit crystals continue to possess in common one degree of orientation in that they have similar, *i.e.*, cube, faces in contact, the respective cube edges in the specimen plane are not parallel but inclined at 45° to each other, with the result that (110) and (100) planes normal to the specimen film in substrate and deposit respectively are parallel to each other. This is clearly a case of a substrate influence complied with by the deposit in such a manner as to lead to as strain-free an arrangement of the atoms in the substrate-deposit interface as possible. Thus, in the pattern, Fig. 9, the gold and iron spacings are such that the 200, 220, etc., gold diffractions coincide with 110, 200, etc., of iron respectively, and it is not until the 11th pattern ring that an iron diffraction, the 123 ring, is obtained free from a gold ring. This means that the cube faces of the iron crystals fit closely on those of the gold substrate when cube corner atoms of iron bisect gold cube edges. When given already one common direction, *i.e.*, (100), of orientation, it is clear that no other arrangement will enable the two structures to fit together so accurately without lattice distortion. It may therefore be concluded that this arrangement of substrate and deposit is also the most strain-free. We have, indeed, observed that iron electrodeposited on a massive gold substrate exhibits exceedingly good adhesion.

In the case of iron electrodeposited on palladium, the two structures fit together in a corresponding manner and, although the fit is not so good as in the case of iron and on gold, it is nevertheless still the best possible under the circumstances.

The remarkable pattern of spots immediately surrounding the undiffracted beam spot in Figs. 7 and 8 is a more or less prominent feature in all the patterns obtained from these composite films in which the substrate produced a pattern approaching to the cross-grating type and therefore practically consisted of a single crystal, or at least of closely packed crystals possessing two well-defined directions of orientation in common.

The origin of this central pattern may be deduced as follows: Owing to the thinness of the composite film, the third Laue condition for diffraction is virtually completely relaxed, and we may regard the specimen as consisting of two superimposed cross-gratings, one of platinum, $a = 3.91 \text{ \AA}$, and the other of copper, $a = 3.61 \text{ \AA}$. Suppose a beam, hkl_{Pt} , from the first cross-grating be diffracted by the underlying copper film, then a complete copper cross-grating pattern should be ascribed about the hkl_{Pt} diffraction spot. Thus, as in Fig. 10, there will be a ray, A, diffracted radially inwards and another, B, radially outwards from the central spot, the distance of A and B from hkl_{Pt} being the radius of the hkl_{Cu} ring. Similarly, other rays, C and D, etc., will be diffracted in various directions from that of the initial hkl_{Pt} ray. So far we have only considered a single platinum crystal with its underlying layer consisting of a copper single crystal in similar orientation; but the patterns, Figs. 7 and 8, consist of a series of short arcs, and we must therefore consider the effect of rotating the cross-gratings about the primary beam by an angle equal to the angular extent of the arcs of the normal pattern. Quite clearly the effect upon A and B will be to spread the spots over an angle, α , subtended by the normal pattern arcs at the central spot. Since A is much nearer the central spot than B, it follows that the same amount of energy will be concentrated into a much smaller area at A than at B. The arc A will therefore be much more intense than B. A similar effect will occur for C and D, but in addition there will be a two-dimensional spreading and consequent blurring of the C and D arcs, owing to the extent of the primary hkl_{Pt} arc, and we should therefore hardly expect to observe such diffractions in the patterns.

This view, according to which the central pattern is due to double diffraction, is completely in agreement with the facts. Thus, in Fig. 7,

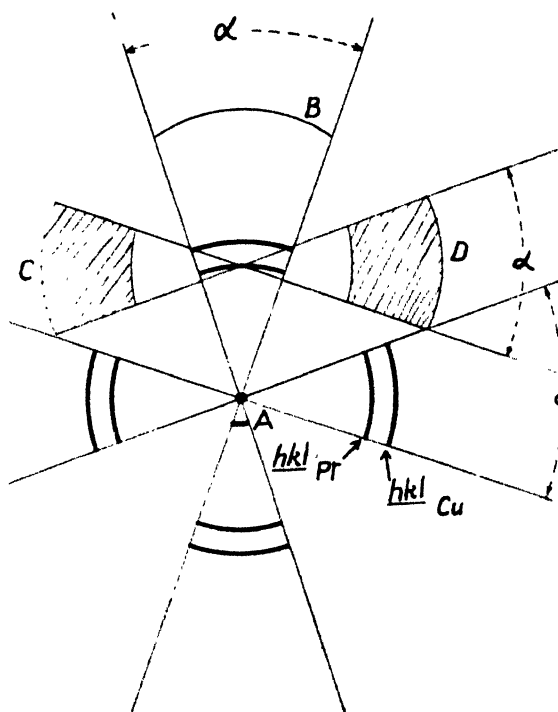


FIG. 10.

the pattern close to the central spot corresponds to a face-centred cubic structure, $a_0 = 48.9$ Å., in exactly the same orientation as the platinum and copper, and the scattering angle corresponding to each of these inner arcs is the difference between the scattering angles of the corresponding diffractions of the platinum and copper respectively. For example, the radius of the arc ascribed to the 111 diffraction from the face-centred cubic structure of cube edge 48.9 Å. is equal to the difference between the radii of the 111 platinum and copper diffractions respectively. Again, all three arcs fall on the same radius and

have the same angular extent, and whilst the arcs near the undiffracted beam spot are intense, the corresponding arcs described about, and on the opposite side, of the 111 platinum diffractions are too weak to be seen in the reproduction, though plainly visible in the original negative.

Similar results obtained with other composite films are set forth in Tables V *a*, *b*, *c*, and *d*. They completely confirm the above double scattering view.

In addition to those shown in Table V*a*, three other arcs foreign to either platinum or copper were observed in the pattern. Their origin could be traced to double diffraction. Thus, the arc with radius 1.14 cms. is due to the diffraction of the 222_{Pt} diffraction by $(111)_{Cu}$ (calculated 1.13 cms.); 1.43 cms. arc due to the diffraction of 111_{Pt} by $(222)_{Cu}$ (calculated 1.43 cms.); and 1.92 cms. arc due to the diffraction of the 200_{Pt} beams by $(331)_{Cu}$ (calculated 1.92 cms.).

Three other arcs were also observed in the pattern of Table V*b*. The arc with radius 1.03 cms. is due to the diffraction of 222_{Pt} by $(111)_{Ni}$ (calculated 1.02 cms.); 1.40 cms. arc due to the diffraction of 111_{Pt} beam by $(222)_{Ni}$ (calculated 1.40 cms.); and the 1.98 cms. arc due to the diffraction of the 311_{Pt} beams by $(440)_{Ni}$ (calculated 1.97 cms.).

The occurrence of this phenomenon of double scattering is of particular importance in connection with the general interpretation of the relative intensities of the diffractions in electron diffraction patterns. In the case of a specimen consisting, for example, of a chaotic aggregation of the same type of crystals, the effect must give rise to an anomalous intensity distribution, in that it will have the tendency to even out the intensity differences between the various diffractions.

TABLE V.—DOUBLE DIFFRACTION BY COMPOSITE FILMS.

Indices of Diffractions.	Radii in cm.	Calculated Differences between Radii in cm.	Observed Radii of Inner Secondary Diffractions in cm.	Calculated Sum of Radii in cm.	Observed Radii of Outer Secondary Diffractions in cm.
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(a) Copper on Platinum (Fig. 7).

111 _{Cu}	1.33	0.10	0.10	2.56	2.56
111 _{Pt}	1.23				
200 _{Cu}	1.52	0.11	0.11	2.94	2.94
200 _{Pt}	1.41				
220 _{Cu}	2.17	0.17	0.17	4.17	—
220 _{Pt}	2.00				

(b) Nickel on Platinum (Fig. 8).

111 _{Ni}	1.27	0.13	0.13	2.41	2.41
111 _{Pt}	1.14				
200 _{Ni}	1.47	0.14	0.14	2.80	—
200 _{Pt}	1.33				
220 _{Ni}	2.08	0.21	0.21	3.95	—
220 _{Pt}	1.87				

(c) Copper on Palladium.

220 _{Cu}	1.55	0.10	0.10	3.00	3.00
220 _{Pd}	1.45				

(d) Cobalt on Platinum.

Faint, diffuse double diffraction pattern observed near and around the central spot.

In the examples of double scattering set forth above, the relationship between substrate and deposit crystal orientation was so intimate that the specimens could be regarded as being virtually single structures but characterised by an abrupt change of lattice constant occurring at a sharply defined boundary within the structure. We should therefore expect to find similar intensity-levelling double-scattering effects even in the case of single crystal transmissions of the cross-grating type. The effect must occur; otherwise it would be difficult indeed to account for the exceptional intensity of the higher order diffractions which is so characteristic of the electron diffraction cross-grating pattern. Thus, it is by no means unusual to record as many as 15 orders in a mica transmission. Beeching⁹ has observed a similar effect in the case of the reflection of electrons from a natural diamond face, and other investigators, notably Raether,¹⁰ have recorded similar anomalies. Bethe's¹¹ dynamical treatment neglects the experimental fact of the co-existence of several strong diffracted beams and their consequent interactions and must therefore be inadequate in its present form as a guide to the quantitative interpretation of intensity distribution. The need for caution at the present time in assigning anything more than a general qualitative significance to intensity measurements of electron diffraction patterns is evident.

⁹ Beeching, *Phil. Mag.*, 1931, **20**, 841.

¹⁰ Raether, *Z. Physik.*, 1932, **78**, 527.

¹¹ Bethe, *Ann. Physik.*, 1928, **87**, 55.

7. Orientation Changes Subsequent to Substrate Removal.

Experiments were carried out with the object of seeing to what extent, if any, the orientation of the deposit crystals might be affected by the removal of the substrate. That such an effect can and does occur is strikingly demonstrated by the patterns, Figs. 9, 11 and 12. Thus, in Fig. 9, from iron electrodeposited on gold, the arcing shows that both metals were in cube face orientation and with an iron cube face parallel to gold cube-diagonal planes. This specimen was next floated, gold downwards, for a few seconds on a weak cyanide solution and re-examined after washing. The resulting pattern, Fig. 11, shows that much of the gold had gone into solution, and that the arcing of the rings has become much less distinct than previously in Fig. 9. After further etching, leaving only a trace of gold, the pattern, Fig. 12, was obtained. The rings are now practically free from arcs, thus showing that with removal of the substrate the second direction of orientation of the iron crystals has been lost. Furthermore, the intensity distribution is now such as to suggest that what slight degree of orientation still remained was (110) rather than (100) parallel to the specimen plane. It is probable that the loss in orientation was due to crinkling of the iron film on removal of the substrate.

We have in other cases observed distinct signs of similar changes due to removal of the substrate influence, but in none were the effects so clearly in evidence as with iron on gold.

8. Substrate Influence on Crystal Size.

An example of the effect of the substrate structure on the crystal size of a deposit has previously been given in the case of chromium electrodeposited on copper, nickel, iron, tin and bismuth substrates.⁴ The size of the deposit crystals appeared to be determined mainly by the crystal size in the substrate, provided the deposition conditions were otherwise the same. Nickel seemed on the whole to be less susceptible than chromium to this specific substrate influence, and generally gave patterns which are remarkable for their clarity and ring definition. Electrodeposited on amorphous arsenic, however, even nickel exhibited a pronounced tendency to form small crystals.

9. Transmission Specimens of Single Metals.

These specimens were prepared in the manner outlined in Table I. and § 5, and had been electrodeposited on basis metals with normal crystal orientations characteristic of the deposition conditions previously outlined. After stripping and removal of the basis metal the films yielded excellent patterns, representative examples of which have previously been reproduced.⁴ It will suffice to recall that it was found that body-centred cubic structures such as iron and chromium tended towards {111}, and the face-centred cubic metals towards {110} orientation.

10. Metal Films formed by Chemical Displacement.

A copper film, either commercial leaf or electrodeposited, rapidly whitened when floating on a 1.0 per cent. acid platinum bi-chloride solution. After immersion in 3*N* nitric acid to remove any unattacked copper, the film yielded a face-centred cubic pattern. Double-shutter comparison with gold showed that the film formed by displacement had lattice constants intermediate between those of platinum and copper, and this was independently verified by the pattern, Fig. 13, obtained from a similar platinum-displaced-by-copper film superimposed on gold.

Similar results were obtained with platinum, displaced by floating a silver film on the platinum salt solution, followed by washing with a dilute ammonia solution and 1½ hours' treatment in 3*N* nitric acid to remove

silver chloride and unattacked silver. A typical double-shutter pattern with gold is shown in Fig. 14, from which it will immediately be evident that the lattice constants of the displaced film lay between those of platinum and silver. This film gave a positive test for silver with *p*-dimethylaminobenzal-rhodamine, and the two platinum-displaced-by-copper specimens, on testing for copper with sodium-diethyl-dithio-carbamate also yielded a similar result.

The lattice constants of the 20 copper-platinum specimens examined lay between 3.71 and 3.77 Å. Similarly, in the case of platinum displaced by silver, the lattice constants were found to vary between 3.97 and 4.05 Å, and it was observed that the lattice constant decreased with the time of contact of the silver with the platinum solution. Thus, the chemical and structural evidence both show that copper-platinum and silver-platinum alloys are formed when thin copper and silver films chemically displace platinum, a result which is in sharp contrast to that obtained in the case of electrodeposited single and double films, where no signs of alloying could be detected.

Summary.

The structure of electrodeposited and chemically displaced metal surfaces and films has been studied by the method of electron diffraction.

It has been found that the structure of the substrate upon which a metal is electrodeposited nearly always profoundly affects that of the deposit, in that the orientation of the substrate crystals determines that of the deposit. In those few cases where the effect did not occur the deposit generally exhibited poor powers of adhesion.

Anomalous diffraction effects, shown to be due to secondary elastic scattering, have been obtained, and the bearing of this phenomenon on the interpretation of electron diffraction pattern intensities has been discussed.

It has been shown that, unlike in electrodeposition, chemical displacement of one metal by another leads to the formation of an alloy.

In this communication we have confined ourselves to setting forth the facts brought to light in the course of experiments and to drawing therefrom the outstanding conclusions of fact. We are deferring a more detailed discussion until the completion of further work which is now in hand.

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THE DIFFRACTION OF ELECTRONS BY AMALGAM FILMS.

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§ 1. Introduction.

The occurrence of isolated so-called "extra" or "forbidden" rings in electron diffraction photographs, more particularly from metal films and surfaces, has long been noted. Such rings were obtained in profusion by Finch, Quarrell and Wilman¹ from both beaten and electrodeposited metal foils, and more especially from such films after heating in contact with various gases followed by rapid quenching to room temperatures. In addition to "extra" rings, these experiments also often led to the appearance of remarkable band systems which were interpreted as evidence of a gradual lattice expansion with entry of gas. These results suggested that the diffraction of high speed electrons might afford a powerful and direct means for investigating the interaction of gases and solids. For the successful prosecution of such a study, however, it would be essential to exclude the formation of "extra" rings due to causes other than gas absorption, or at least to be able to recognise the origin of such rings when they do occur.

Mark, Motz and Trillat² have shown that traces of grease can give rise to a well-marked group of "extra" rings in patterns from metal films and also from cellulose. The corresponding spacings, however, have been found to be independent not only of the nature of the metallic or cellulosic substrate but also of the types of grease so far found to occur as adventitious impurities in the laboratory. "Grease" ring systems should therefore not be difficult to recognise. Furthermore, by taking suitable precautions the formation of such contaminating grease layers can be suppressed; also, as Trillat³ has pointed out, the grease can generally be removed by washing the specimens with suitable solvents.

Finch and Quarrell⁴ have recently recorded the fact that amalgamation can give rise to "extra" ring systems which, unlike the grease rings, have spacings dependent upon the metal and are thus more difficult to distinguish from absorbed gas rings than are the grease rings with their constant spacings. The following experiments were therefore carried out with the object of elucidating the structure of thin gold, silver, copper and palladium foils after attack by mercury under conditions which could be considered as representative, even though possibly exaggerated, of adventitious contamination of such films in the laboratory.

¹ Finch, Quarrell and Wilman, *Trans. Faraday Soc.*, 1935, **31**, 1051.

² Mark, Motz and Trillat, *Naturwiss.*, 1935, **20**, 319.

³ Trillat, *Trans. Faraday Soc.*, 1935, **31**, 1127.

⁴ Finch and Quarrell, *Nature*, 1935, **136**, 720.

§ 2. Experimental.

Gold, silver, palladium and copper were supplied in leaf form by Messrs. G. M. Whiley Ltd. The gold was described as "fine gold, guaranteed absolutely free from alloy." After thinning by floating on a $N/50$ potassium cyanide solution, followed by washing in distilled water, it gave diffraction patterns characteristic of the pure metal, except that in addition to the normal rings at least two "extra" rings corresponding to spacings of 4.44 and 2.56 Å. were more or less faintly discernible in the majority of specimens taken from three books of two different batches. It will be seen later that these "extra" rings were due to traces of amalgamation. The gold crystals were generally orientated with (100) planes parallel to the film (complete rings with the specimen normal to the beam, but the 200 very strong and 111 abnormally weak) and frequently a second common direction of orientation was also more or less in evidence, the rings tending to break up into arcs. The "extra" rings, however, were always continuous.

According to Messrs. Whiley, silver does not beat into a fine leaf unless of a high grade of purity. The leaf supplied assayed over 99.9 per cent., the chief impurity being copper with traces of arsenic and lead. The cyanide-thinned and washed leaf gave the normal silver pattern, usually free from any signs of "extra" rings. In most specimens the crystals were orientated in the manner observed in the case of gold, the diffraction rings being more or less strongly curved.

The palladium leaf was beaten from a high grade metal obtained from the Mond Nickel Company. It was thinned by floating on a solution of concentrated nitric acid in an equal volume of water and washed as above. The patterns were characteristic of palladium and free from "extra" rings. The crystals were more highly orientated than in the case of gold or silver, and many specimens yielded a nearly perfect cross-grating pattern characteristic of cube face orientation.

The copper leaf had been beaten from electrolytic metal and contained only traces of impurities, chiefly lead and arsenic. It was thinned with an acidified solution of ammonium persulphate or with a 20 per cent. potassium cyanide solution and washed. The patterns were typical of copper, though occasionally a much fainter secondary ring system due to cuprous oxide appeared.

Amalgamation was carried out by hanging a 3×1.5 cm. strip of the thinned leaf above a warmed drop of mercury until the lower edge had been whitened, in the case of gold, or become brittle and frosty in appearance in the case of silver. Palladium showed no visible signs of attack even after prolonged exposure leading to condensation of mercury on the leaf. Copper amalgam specimens prepared in this manner were found to be unsuitable for electron diffraction.

Amalgamation was also carried out by electrodeposition and by chemical displacement. Thus gold leaf was amalgamated by using it as a cathode in a nearly saturated mercuric chloride bath with a mercury anode. By varying the current density and times of deposition a wide control of the extent of amalgamation could be effected. Silver amalgams were similarly prepared with mercuric chloride and nitrate baths. Finally, silver and copper amalgams were obtained by merely floating the leaf on such baths, the extent of attack being controlled by the time of contact.

§ 3. Gold Amalgams.

The gold leaf specimens attacked by mercury vapour exhibited all shades of colour from that of pure unalloyed gold to the metallic white of the mercury-rich amalgam formed at the lower edge of the leaf. The transition from yellow to white occurred rapidly, however, and was confined as a rule to a strip of about only 1 mm. width. Diffraction patterns were taken from several places in and on either side of this transition zone.

Patterns from the gold side were characteristic of gold except for the appearance of two comparatively strong amalgam rings lying inside the 111 gold diffraction and corresponding to spacings of 4.44 and 2.56 Å., and which are nearly always visible in most gold leaf patterns. Although the gold rings were arced, the amalgam rings were always continuous. On progressing towards the mercury-rich end of the specimen, these "extra" rings became more and more prominent (Fig. 1), many new rings appeared and, with further approach to the most heavily amalgamated area, some of these in turn disappeared whilst others became stronger until the gold pattern was completely displaced by a fully developed amalgam ring system which must be due to a well-crystallised gold-mercury alloy (Fig. 2). The spacings corresponding to the gold amalgam rings, referred to gold,

TABLE I.—GOLD AMALGAM ($a_{Au} = 4.070 \text{ Å.}$).

Spacings, Å.	Ring Intensities.	Assigned Indices.	Spacings Calculated for a Simple Cubic Lattice, $a = 17.81 \text{ Å.}$
4.44	v.s.	400	4.45
2.94	f.	600	2.95
2.60	f.m.	631	2.60
2.56	s.	444	2.57
2.49	m.s.	$\begin{Bmatrix} 551 \\ 711 \end{Bmatrix}$	2.49
2.39	f.	642	2.38
2.23	m.	800	2.23
2.19	v.f.	$\begin{Bmatrix} 741 \\ 811 \\ 554 \end{Bmatrix}$	2.19
2.06	f.; d.	$\begin{Bmatrix} 555 \\ 751 \end{Bmatrix}$	2.06
1.69	m.	10, 31	1.70
1.60	f.	10, 50	1.59
1.50	m.	10, 62	1.50
1.49	m.	12, 00	1.48
1.47	m.	777	1.47
1.44	m.	10, 64	1.44
1.30	m.	13, 33	1.30
1.24	f.m.	10, 10, 2	1.25

In column 2 the diffracted intensities are recorded as v.s. = very strong, s. = strong, m.s. = medium strong, m. = medium, f.m. = faint to medium, f. = faint and v.f. = very faint; d. signifies diffuse.

as to render it difficult to assign definite structures to the intermediate alloys. Further, out of 20 patterns yielded by incompletely amalgamated gold specimens, no two patterns containing four or more amalgam rings agree throughout either in ring diameters or intensities, a fact which testifies to the remarkably wide range of structures to be met with in the incompletely amalgamated gold specimens.

The amalgams formed by the electrodeposition of mercury on a gold leaf cathode were prepared with the object of obtaining evidence of the possible formation of amalgams differing from the above structure observed when the leaf had been fully attacked at room temperature by mercury vapour. Though in all 15 such specimens, representative of a wide range of colour between gold and mercury-white were prepared, the resulting patterns confirmed in every relevant detail the results obtained in the case of attack by mercury vapour.

$a_{Au} = 4.070 \text{ Å.}$, are given in Table I. The best fit we have been able to find is given by a simple cube of $a = 17.81 \text{ Å.}$ No space-group can be assigned, as the pattern does not afford sufficient information, and we have not succeeded in obtaining single crystal patterns.

It seems likely that the mercury-richest of the gold amalgams was also the most stable of those examined. Thus several rings, notably the two very intense ones corresponding to 4.44 and 2.56 Å. which were the first to appear in the initial stages of amalgamation, persisted right through into the patterns from the fully amalgamated specimens; whilst the appearance and disappearance of other rings with progressing amalgamation afforded evidence of the transitory formation of a wide range of intermediate alloys. The complexity of the corresponding patterns is such

In addition to the above outlined methods of preparing gold amalgam, we have found that heating a partially amalgamated gold film to a sufficiently high temperature in vacuo leads to the formation of the amalgam structure described in Table I. Thus, a fresh gold leaf specimen which only faintly showed the two normally most prominent amalgam rings, after 15 mins. heating in vacuo at 720° yielded a pattern similar to Fig. 2 and without any trace of gold rings. The pattern could only be obtained, however, from a few small areas of the specimen, the heat treatment having otherwise resulted in the collapse of most of the gold film previously bridging the meshes of the supporting gauze, probably as a result of melting. Thus Faraday⁵ found that a continuous gold film on glass gathered up into minute globules on heating at 300° . Hence it seems that, from the point of view of electron diffraction, the gold is destroyed as a specimen by a heat treatment which is successfully resisted by the amalgam films. This and other similar results are of importance in connection with the study of the absorption of gases by metallic foils, in that they show how easily an originally practically negligible concentration of amalgam may virtually increase, as a result of heating, to such an extent as finally to predominate in imposing its character upon the diffraction pattern.

These experiments were repeated with fresh gold films formed by electro-deposition in the manner previously outlined.¹¹ Such films proved to be free from mercury in that they afforded no trace of amalgam rings even after prolonged heat treatment, provided this was carried out in a vacuum free from mercury vapour.

Pabst⁶ and Stenbeck⁷ have investigated the gold-mercury system by means of X-ray diffraction, using carefully annealed specimens. No agreement has been found between their results and those obtained in these experiments.

§ 4. Silver Amalgams.

It was not easy to obtain sufficiently robust and yet not too dense amalgamated silver specimens by mercury-vapour attack of suitably thinned leaf, largely owing to the patchy and uneven thickness of the raw leaf. Also it was more difficult than in the case of gold to distinguish visually the transition between the fully amalgamated to un-attacked silver. As before, however, patterns were obtained through areas likely to be representative of progressive attack by gradually working from the upper to the lower leaf edge. After slight amalgamation, two fairly prominent continuous amalgam rings with spacings of 2.92 and 2.44 Å. appeared within the silver 111 diffraction.

TABLE II—SILVER ($a_{\text{Ag}} = 4.077$) AMALGAMATED BY MERCURY VAPOUR.

Spacing, Å.	Ring Intensities.	Assigned Indices.	Spacings Calculated for a f. c. Tetragonal Lattice, $a = 6.93$ Å, $c = 5.82$ Å, $c/a = 0.84$.
3.77	m.	111	3.75
2.92	s.	002	2.91
2.44	m.s.	220	2.45
2.22	f.m.	202	2.23
2.05	m.	131	2.05
1.87	v.f.	222	1.87
1.81	m.	113	1.80
1.57	m.	331	1.57
1.48	f.m.	402	1.49
1.42	f.m.	004	1.45
1.26	v.f.	251	1.26
1.13	v.f.	442	1.13
1.02	v.f.	301	1.02

A fully attacked area gave the pattern, Fig. 3, containing no silver rings, and in which the two inner amalgam rings have become much stronger.

⁵ Faraday, *Phil. Trans.*, 1857, 147, 145.

⁶ Pabst, *Z. physik. Chem. (B)*, 1929, 3, 443.

⁷ Stenbeck, *Z. an. all. Chem.*, 1933, 214, 16.

The analysis of Fig. 3 is given in Table II. A reasonably good fit is given by a face-centred tetragonal structure, $a = 6.93$ and $c = 5.82$ Å.

The structure assigned above should give a 200 diffraction; its absence, however, might well be due to a general tendency of the crystals to orientate with (100) planes parallel to the specimen plane. This view is borne out by the pattern, Fig. 4, in which, however, in addition to the rings corresponding to the spacings set forth in the first column of Table II, there appears a ring of medium intensity with the spacing 3.43 Å., the theoretical value for 200 indexing being 3.46 Å. In this case the silver specimen had been prepared by electrodeposition from a cyanide bath and had (110) orientation before amalgamation.

The initial stages of amalgamation by electrodeposition of mercury on silver from mercuric nitrate were found to be marked by the appearance of two prominent "extra" rings inside the 111 diffraction and with spacings nearly similar to those first developed in the early stages of the amalgamation of gold. After electrodeposition at 0.1 A./dcm. during 40 seconds, a pattern containing only amalgam rings was obtained. The analysis is

TABLE III.—SILVER AMALGAMATED BY ELECTRO-DEPOSITED MERCURY.

Spacings, Å.	Ring Intensities.	Assigned Indices.	Spacings Calculated for a Simple Cube, $a = 17.94$.
4.48	s.	400	4.49
3.90	v.v.f.	421	3.91
3.51	f.	510	3.52
3.18	v.v.f.	440	3.17
2.86	v.f.	620	2.84
2.59	v.s.	444	2.59
2.51	f.m.	551	2.51
2.38	m.d.	642	2.40
2.24	m.	800	2.24
2.21	m.	811	2.21
2.06	f.d.	662	2.06
1.85	f.d.	932	1.85
1.70	m.	3.1.10	1.71
1.65	m.	3.3.10	1.65
1.51	m.s.	5.4.10	1.51
1.45	m.s.	7.2.10	1.45
1.30	m.s.	3.3.13	1.31
1.25	m.	2.10.10	1.25

given in Table III, from which it will be seen that this silver amalgam is closely similar to that obtained from gold amalgamated by mercury vapour, Fig. 2, and thus has a structure practically identical with that of the final gold amalgam; indeed, owing to the similarity between the lattice constants of gold and silver, it would be difficult to distinguish between the two amalgam patterns without double-shutter measurements.

An amalgam of similar structure was also obtained by displacing silver from a nearly saturated silver nitrate solution by a drop of mercury. The resulting amalgam after washing and supporting on a collodion film spanning nickel gauze gave a pattern similar to that analysed in Table III.

Silver leaf after floating on a nearly saturated mercuric chloride solution during three minutes gave complex ring patterns containing no silver rings. The analysis of the representative pattern, Fig. 5, is set forth in Table IV. Similar patterns were also occasionally obtained from specimens amalgamated by electrodeposition. We have so far not succeeded in clearly defining the conditions of electrodeposition leading to either this or the former type of amalgam yielding a pattern similar to that analysed in Table III.

Hence the structure of this silver amalgam was probably face-centred tetragonal, $a = 9.05$ Å., $c = 5.62$ Å., $c/a = 0.62$, and thus differed entirely from that of the gold and the two silver amalgam structures described above.

The commercial silver leaves used in these experiments were as a rule less contaminated by traces of mercury than the gold. Thus it was only in exceptional cases that the 4.48 and the 2.57 Å. amalgam rings were visible in a pattern from the fresh leaf, and then only faintly. Nevertheless,

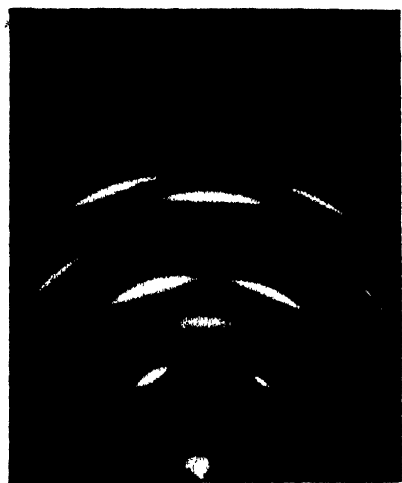


FIG. 1 Fe on polished Cu
(111) orientation



FIG. 2 Au on polished Cu.
(111) orientation.

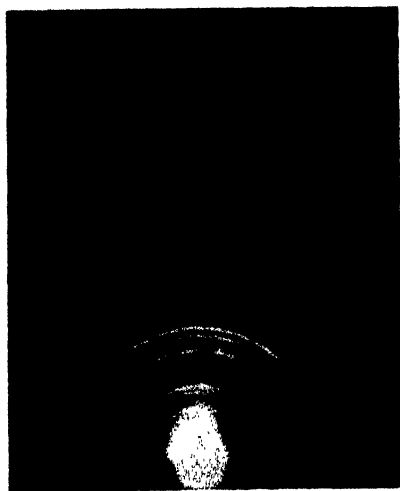


FIG. 3. -Bi on polished Cu.
Unorientated.

[See page 854.



FIG. 4.—Fe on (110) Ni.
(100) orientation.



FIG. 5 Fe on (111) Au.
(110) orientation

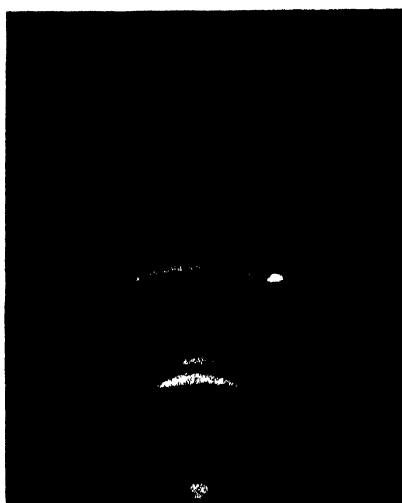


FIG. 6.—Cu on (111) Au.
(111) and (100) orientations.

[See page 855.

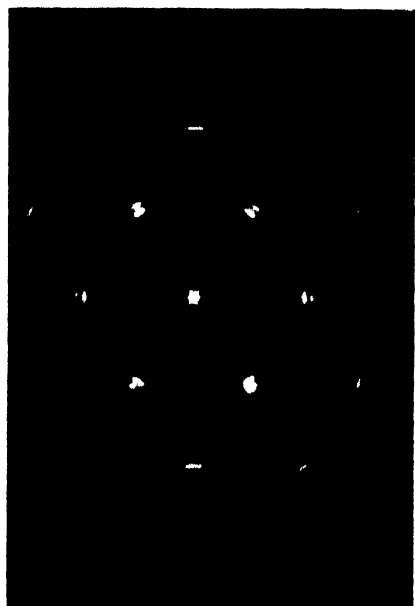


FIG. 7. Cu on (110) Pt. (110) orientation. Note central spot pattern.

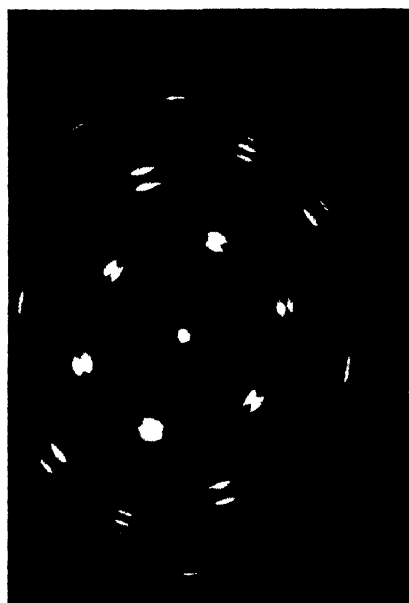


FIG. 8. Ni on (110) Pt. (110) orientation. Faint central spot pattern.

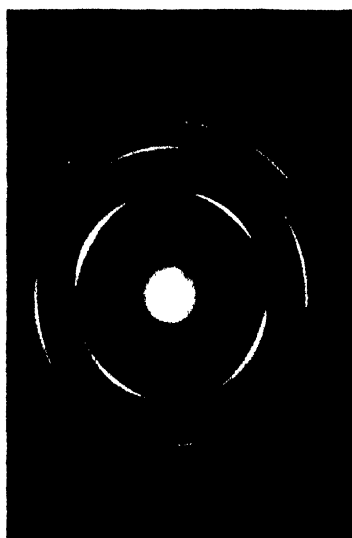


FIG. 9. Fe on 100 Au.
[See page 858.]



FIG. 11. As in Fig. 9, but after partial removal of Au

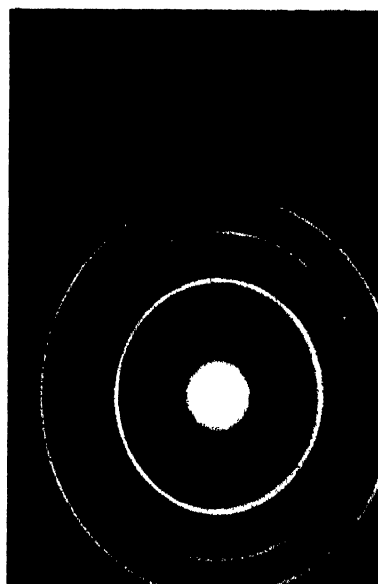


FIG. 12. As in Figs. 9 and 11, but Au almost completely removed
[See page 862.]

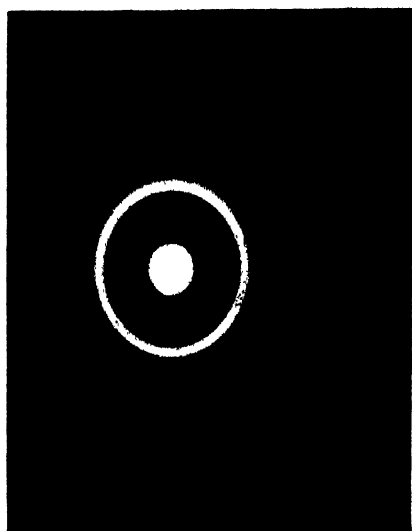
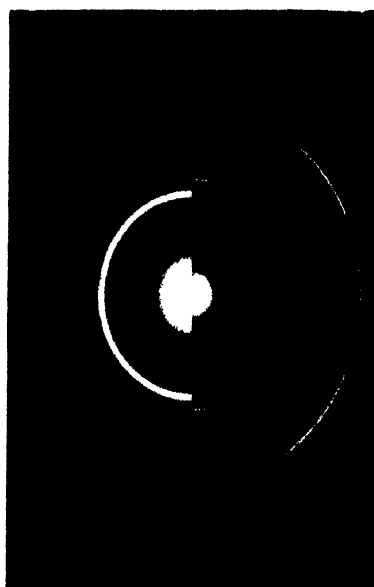


FIG. 13.---Pt-Cu alloy superimposed on Au.



Pt-Ag Au
FIG. 14.---Pt-Ag alloy and Au comparison pattern.
[See page 863.]

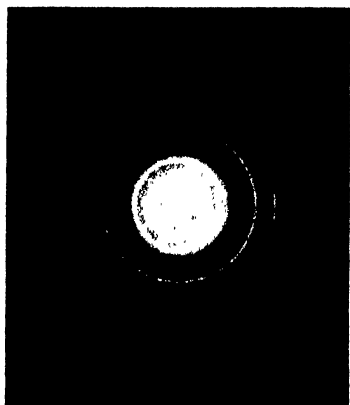


FIG. 1. Partially amalgamated Au

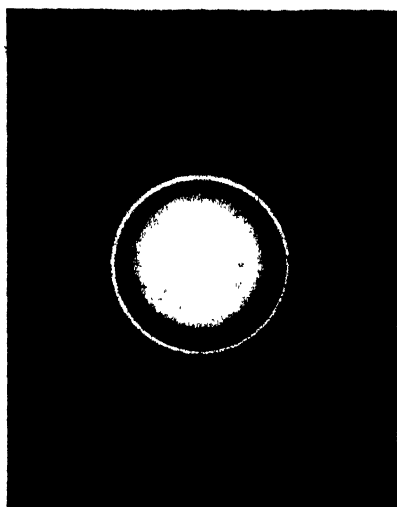


FIG. 2.—Completely amalgamated Au.

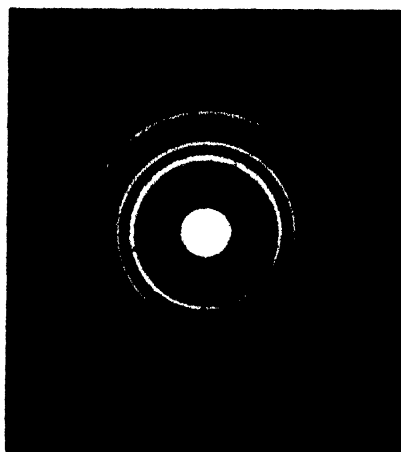


FIG. 3. Completely amalgamated Ag;
specimen normal to beam

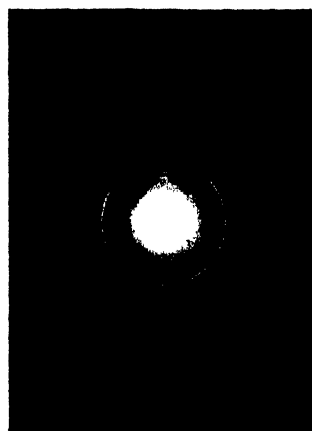


FIG. 4. Completely amalgamated
electro-deposited Ag.

[See page 866.

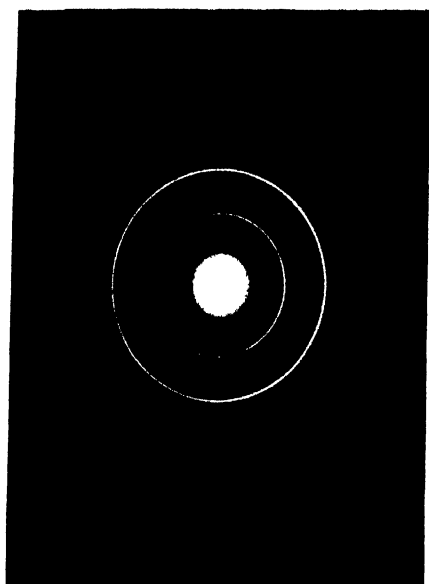


FIG. 5 Ag amalgamated by chemical displacement.

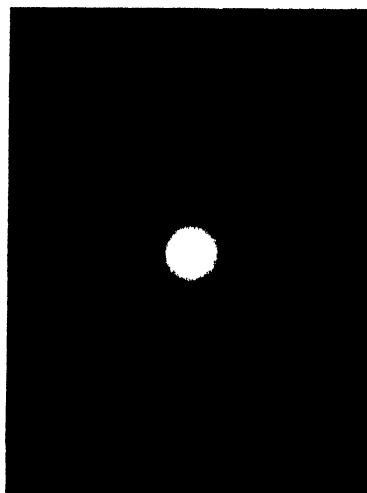


FIG. 6 Ag amalgam formed by heating partially amalgamated Ag leaf at 140.

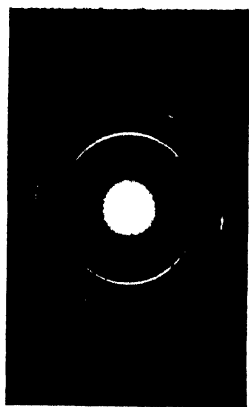


FIG. 7. Partially amalgamated Cu.

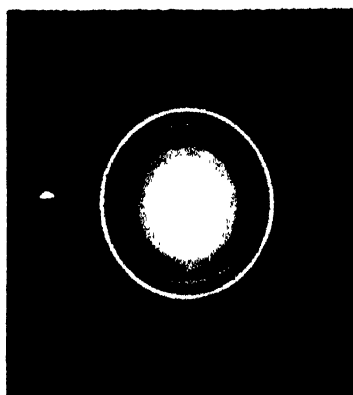


FIG. 8 Completely amalgamated Cu.

[See page 868.

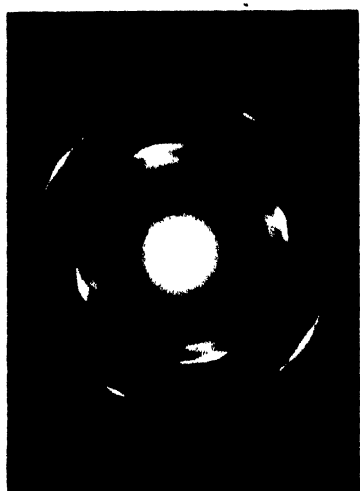


FIG. 9. Pd after slight exposure to Hg vapour

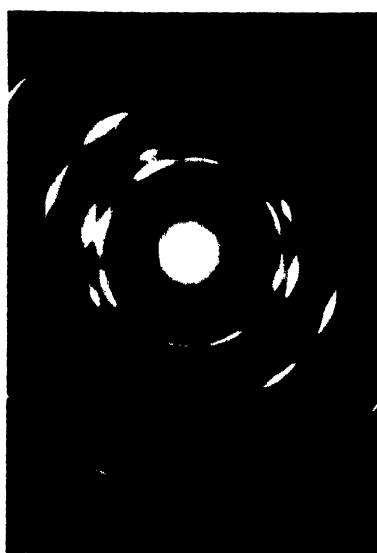


FIG. 10. -Pd after long exposure to Hg vapour.

[See page 870.

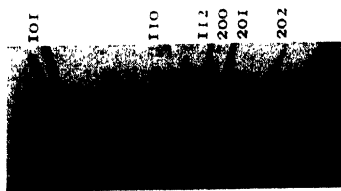


FIG. 1.—Anticathode-Fe. The X-ray beam striking the sample at a 30° angle. Zn with 4 gm. of dextrine per litre. 4 amp./ cm^2 , 20 min.

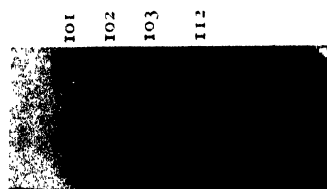


FIG. 2.—Cd with 0.5 gm./l. of cereals extracts, $\angle 30^\circ$.

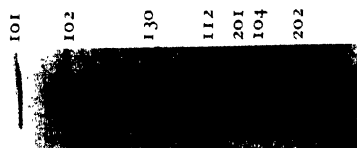


FIG. 3.—Zinc deposited without colloids, $\angle 47^\circ$.

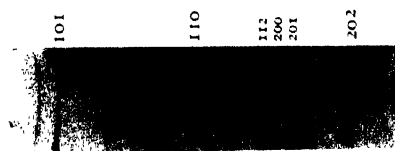


FIG. 4.—Zn with 2 gm./l. dextrine, 5 amp./ cm^2 , 10 mm., $\angle 47^\circ$.

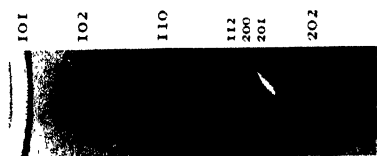


FIG. 5.—Zn with 2 gm./l. dextrine, 2 amp./ cm^2 , 40 mm., $\angle 47^\circ$.

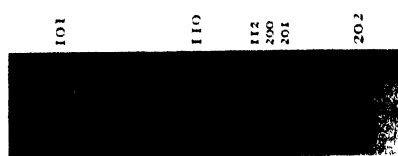


FIG. 6.—Zn with 10 gm./l. of dextrine, $\angle 47^\circ$.

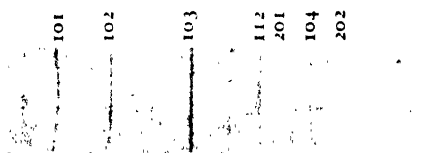


FIG. 7.—The plate of Zinc, $\angle 47^\circ$. Anticath.-Fe.

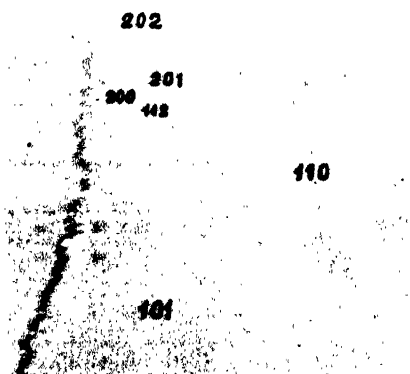


FIG. 8.—Microphotogram of Zinc deposited in the presence of dextrine.

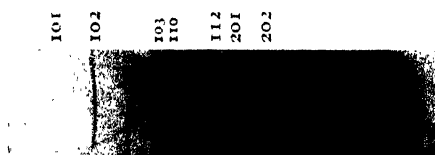


FIG. 9.—Cd deposited in the presence of dextrine. Anticathode-Fe, $\angle 47^\circ$.

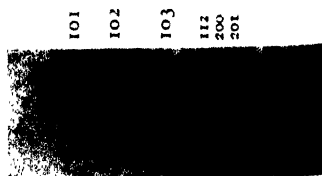


FIG. 10.—Cd with 1 gm./l. of cereals extracts.

[See page 940.

even in the case of a leaf which initially had yielded a normal silver pattern free from amalgam rings, heating at 190° during 15 minutes in a mercury-free vacuum maintained by an oil vapour pumping equipment led to the appearance of many amalgam rings corresponding to the spacings given in Table III; indeed, many of these amalgam rings were obtained from a specimen after heating at only 140° during 15 minutes (Fig. 6); after 2 minutes at 600° the original silver pattern had been displaced by a pattern virtually identical with that from which Table III was compiled. In this case it is possible that the concentration of the slight traces of amalgam which must have been present in the original leaf was due to the evaporation of the silver rather than to the disruption of the film by fusion, because it is well known that thin silver films sublimate readily at temperatures in excess of about 300° .

As in the case of gold, X-ray investigation of the silver-mercury system by Murphy and Preston,⁶ Stenbeck,⁷ and Weryha⁸ has yielded results which differ from those recorded above

TABLE IV.—SILVER AMALGAMATED BY CHEMICAL DISPLACEMENT.

Spacings, Å.	Ring Intensities.	Assigned Indices.	Spacings Calculated for a f - c , Tetragonal Lattice. $a = 9.05$ Å, $c = 5.62$ Å, $c/a = 0.62$.
4.22	m.	111	4.22
3.23	s.	220	3.20
2.80	m s	002	2.81
2.27	f.	400	2.26
2.09	m	222	2.10
1.99	v.s	331	1.99
1.76	v.f.	402	1.76
1.69	f	151	1.69
1.53	f m	133	1.56
1.50	v f	{ 600 531	{ 1.51 1.49
1.39	v.f	{ 442 004	{ 1.39 1.40
1.29	v.f.	550	1.28
1.25	m s.	640	1.25
1.18	v f	{ 404 603	{ 1.19 1.17
1.14	m.	{ 642 800	{ 1.14 1.13

§ 5. Copper Amalgams.

The copper leaf used in these experiments, after thinning by floating on an acidified ammonium persulphate bath, followed by a cyanide bath to remove cuprous oxide and a final washing in distilled water, gave patterns characteristic of copper, nearly in the form of a thin single crystal in (110) orientation, together with the 111 diffractions of cuprous oxide

TABLE V.—COPPER AMALGAM.

Spacings, Å.	Ring Intensities.
4.99	f.m.
4.11	f.
3.38	m.
2.86	v.s.
2.60	f.
1.71	m.
1.31	f.

The pattern, Fig. 7, obtained with the specimen plane inclined to the beam, shows the result of initial amalgamation effected by floating the thinned leaf on a nearly saturated mercuric chloride solution during 5 seconds, followed by washing in a cyanide bath and in distilled water. In addition to numerous fainter arcs superimposed on the copper pattern, a prominent arced amalgam ring corresponding to a spacing of 2.86 Å. appeared in the earlier stages of attack. The nature of the arcing shows that the amalgam crystals had one common preferred direction of orientation as compared with the two possessed by the original copper specimen; this is confirmed by the pattern, Fig. 8, obtained after complete

⁶ Murphy and Preston, *J. Inst. Metals*, 1931, 46, 501.

⁸ Weryha, *Z. Krist.*, 1933, 86, 335.

amalgamation with the specimen plane normal to the beam. The 2.86 Å. ring is now exceedingly intense and by far the strongest diffraction in the pattern, which contains no copper rings. The spacings and ring intensities are given in Table V. In view of the relatively few diffractions recorded no significant structure can be assigned.

§ 6. Palladium.

The thinned palladium leaf gave good diffraction patterns in which the short arcs and faintness of the 111 diffractions testified to two well-marked degrees of orientation with (100) faces in the specimen plane, the individual crystals aligning up towards the formation of a single crystal.

It might have been thought that, like platinum, palladium would not be affected by mercury at room temperature. The patterns obtained from the leaf after progressive exposure to mercury vapour, however, afforded ample evidence of some form of attack. The initial stage (Fig. 9) was

TABLE VI.—MERCURY ON PALLADIUM.

Spacings, Å.	Ring Intensities.
6.77	v.f.
4.54	f.; d.
3.34	f.
3.02	f.
2.75	f.
2.64	v.f.
2.45	v.f.
2.35	f.
1.58	m.
1.51	f.
1.48	f.
1.34	f.
1.27	f.m.

characterised by the appearance of three rather diffuse rings of which the middle and most intense was just within the 111 palladium diffraction. In the later stages of amalgamation these diffuse rings became sharper and showed signs of resolution into several rings, whilst new and sharp rings appeared for the first time. Finally, the last stage of attack corresponding to saturation of the leaf with mercury was characterised by a multi-ringed pattern superimposed on the normal palladium arc pattern which unlike in the cases of gold, silver and copper, *i.e.* all metals which amalgamate readily, persisted throughout (Fig. 10). Owing to the complexity of this final palladium amalgam ring system no definite structure can be assigned at this stage.

The fact that even a palladium leaf which had been exposed to mercury vapour until completely covered by condensed mercury and then kept in this stage for several hours before examination always gave a far stronger palladium than amalgam pattern suggests either that the attack by mercury

consisted in a surface absorption, rather than in a real amalgamation of palladium itself, or that the amalgam rings are to be ascribed to the amalgamation of impurities contained in the palladium. It is true that the patterns from the fresh palladium leaf showed no trace whatever of any foreign crystal structure, but it may well be that amalgamation suffices to bring into evidence impurities otherwise too slight in amount to affect the main diffraction pattern. The spacings corresponding to the amalgam rings are given in Table VI, referred to palladium, $a_{Pd} = 3.882$ Å.

§ 7. Amalgamation in the Diffraction Camera.

It is now a matter of experience in this laboratory that gold and silver, and possibly also other metals, are prone to amalgamation in an electron diffraction camera evacuated by a mercury vapour pump, no matter whether provided with a liquid-air trap or injector system, particularly when they are in the form of transmission specimens and thus open to attack from two sides.

As a rule with gold the first signs of amalgamation, in the shape of the faint appearance of the most prominent amalgam ring or rings, generally become visible after the specimen has been in the evacuated diffraction camera during about 1 hour; amalgamation then proceeds slowly until, after between about 1 and 2 days' sojourn in the evacuated camera, a gold specimen is usually completely amalgamated. In most cases such slow amalgamation is immaterial because the specimen seldom remains in the

camera during more than 10 or 15 mins. When, however, the specimen is being subjected to some special treatment, such as heating in contact with a gas, either *in situ* in the camera or elsewhere, and which calls for its frequent re-examination, amalgamation may well occur to such an extent as to obscure the issues. Hence in all such work it is essential to conduct the structural examination in a mercury-free vacuum. Two cameras,¹⁰ the one depending for evacuation upon oil vapour pumps alone, the other upon an oil vapour backed by a mercury vapour pump, are available in this laboratory for this purpose and prolonged tests have now shown that no amalgamation of the specimen occurs in either.

§ 8. Conclusions.

It was pointed out in §1 that the main object of these experiments was to obtain the information necessary to permit of the recognition of the so-called "extra" ring systems due to adventitious amalgamation as and when they might occur in patterns obtained from metal specimens heated in contact with gases. The results set forth above, however, make it abundantly clear that amalgam ring systems are in general of such complexity and vary so much between themselves according to the extent to which amalgamation may have proceeded that, unlike grease rings, their identification must always be a matter of uncertainty. Accordingly, in studying by electron diffraction the absorption of gases by metal films and surfaces, it is clearly essential to commence with mercury-free specimens which, as pointed out above, can always be obtained by electrodeposition under suitable conditions,¹¹ and to conduct the further treatment and examination in a mercury-free atmosphere. As a check on the realisation of such conditions, it is now our custom to carry out blank heating experiments and structure determinations with mercury-free transmission specimens of electrodeposited gold, as this metal is the most prone to amalgamation of those which we have so far studied.

§ 9. Summary.

Amalgams of gold, silver and copper and also the effect of mercury vapour on palladium leaf have been studied by electron diffraction.

It has been found that gold and silver readily form a wide variety of amalgam structures of which three have been successfully analysed. Thus gold and silver both form simple cubic amalgams $a = 17.81$ and 17.94 Å. respectively; and two other silver amalgams, both of face-centred tetragonal structure, have also been recognised. Copper also amalgamates readily, particularly during the chemical displacement of mercury, but the structure of the most characteristic amalgam thus formed has not been identified. Palladium is only partially attacked by mercury.

The occurrence and prevention of adventitious amalgamation during the electron diffraction examination and heat treatment of metallic specimens has been discussed.

We wish to thank the Government Grant Committee of the Royal Society and Messrs. Ferranti, Ltd. and Imperial Chemical Industries, Ltd., for grants and apparatus.

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Imperial College of Science and Technology, London.*

¹⁰ Finch and Fordham, *Proc. Physic. Soc.*, 1936, **48**, 85, give a brief description of one such camera.

¹¹ Finch and Sun, *Trans. Faraday Soc.* This vol. p. 852.

A NOTE ON THE THEORY OF VISCOSITY OF LIQUIDS.

BY D. B. MACLEOD, M.A., D.Sc.

Communicated by ERIC K. RIDEAL.

Received 9th March, 1936.

Andrade¹ has developed a theory of the viscosity of liquids in which he arrives at the equations

$$\eta v^{\frac{1}{2}} = A e^{c/T^0}$$

and

$$\eta v^{\frac{1}{2}} = \frac{A'}{\sqrt{K}} e^{c'/T^0}$$

where η is the viscosity of a liquid, v the specific volume, K the compressibility and A , A' , c and c' are constants. The approximate formula $\eta = A e^{c/T}$ has been proposed independently by several authors.

The author has shown^{2, 3} that the viscosity of a liquid can be represented as a function of the free space. Thus if v is the specific volume of a liquid and b the constant volume occupied by the molecules, then

$$\eta = \frac{c}{(v - b)^n} \text{ where } c \text{ is a constant.}$$

For non-associated liquids n approximates to unity but is much greater than unity for liquids usually regarded as associated.

Evidence was brought forward³ to show that the constant c contained the molecular weight as a factor. The departure of n from unity was interpreted as being due to a certain degree of association in all liquids, which changes with rise of temperature, resulting in a change of the effective molecular weight. The equation

$$\eta = \frac{KM \cdot \alpha}{v - b}$$

was suggested, where M is the ordinary molecular weight of the substance and α a quantity greater than unity, depending on the degree of association and, in general, decreasing with rise of temperature.

It is proposed to show that an equation of the type of Andrade can be developed from the above equations.

The Internal Pressure of a Liquid.

The quantity, $v - b$, is intimately connected with the internal pressure of a liquid, by van der Waals' equation

$$(p + \pi)(v - b) = RT$$

¹ *Phil. Mag.*, 1934, 17, 497 and 698.

² "On a relation between the viscosity of a liquid and its coefficient of expansion," *Trans. Faraday Soc.*, 1923, 19, 6.

³ "On a relation between the viscosities of liquids and their molecular weights," *ibid.*, 1925, 21, 151.

For a liquid below its boiling-point, the external pressure p is negligible compared with the internal pressure π , so that, under these conditions we can write

$$\pi = \frac{RT}{v - b}$$

Van der Waals suggested $\pi = \frac{a}{v^2}$ to cover the changes of π with change of volume. Most authors have found it necessary to make a a function of temperature. Berthelot writes $\pi = \frac{a}{Tv^2}$ and Clausius $\pi = \frac{a}{T(v + c)^2}$. None of these quantities when equated to $\frac{RT}{v - b}$, gives a satisfactory agreement over any considerable range of temperature.

The author suggests the expression $\pi = \pi_0 e^{c'/T}$ for the internal pressure of a liquid on the following general argument. The equation $\pi = \frac{a}{v^2}$ assumes that, at any moment, all the molecules are contributing equally to the internal pressure. It is plausible to regard the internal pressure as being almost entirely due to those molecules which, on account of their temporary low velocities—following the Maxwell distribution of velocities—have coalesced with other molecules or are in very close association with them. The internal pressure between two such molecules would be very great compared with that between two average molecules and might correspond to the internal pressure between two molecules in the solid form. It could, in fact, be represented by some constant quantity π_0 . The total internal pressure would then be π_0 multiplied by the number of molecules at any given temperature momentarily in this condition. The number of such pairs, following Maxwell's law, would be an exponential function of the temperature, decreasing with rise of temperature. As a liquid can be solidified by pressure alone, the number would also be a function of the volume. Over the range from the melting-point to the boiling-point, for most liquids, a simple inverse function expresses the facts. The internal pressure of a liquid, from this point of view, is a very generalised type of chemical action, with a very low energy change between a state of combination and a state of freedom. It is only possible under highly compressed conditions, which explains its dependence on volume as well as temperature.

It is proposed to write, therefore

$$\pi_0 e^{c'/T} = \frac{RT}{v - b} \quad . \quad . \quad . \quad . \quad (1)$$

for the change of volume of a liquid with temperature. This expression contains three unknowns, namely $\frac{\pi_0}{R}$, c' and b and is of a form that can only be solved by trial and error. The value of $v - b$ in this equation is identical with that calculated from the equation

$$\eta = \frac{c}{(v - b)^n}$$

The application of equation (1) will be illustrated by octane, for which liquid the experimental data are available over a large range of temperature.

In the previous paper ² the value of $(v - b)$ at 0° C. for octane, calculated from the equation $\eta = \frac{c}{(v - b)^n}$ is given as 0.0940.

Substituting this value of $v - b$, in equation (1) virtually reduces the unknowns to two.

Thorpe and Rodger ⁴ give the following equation for the specific volume of octane.

$$U_t = 1 + 0.02118304t + 0.00186648t^2 + 0.00712947t^3.$$

Table I., column II., gives the volumes at various temperatures calculated from this expression. Column III. gives the free space at various temperatures, assuming b to be constant, e.g., $v - b$ at 120° is

I. Temp. °C.	II. Vol.	III. ($v - b$) _{obs.}	IV. ($v - b$) _{calc.}
0	1.0000	0.0940	0.0953
10	1.0119	0.1059	0.1063
20	1.0238	0.1178	0.1178
30	1.0360	0.1300	0.1298
40	1.0485	0.1425	0.1424
50	1.0612	0.1552	0.1553
60	1.0745	0.1685	0.1683
70	1.0882	0.1822	0.1824
80	1.1025	0.1965	0.1969
90	1.1174	0.2114	0.2118
100	1.1331	0.2271	0.2271
110	1.1496	0.2436	0.2430
120	1.1670	0.2610	0.2592

$$0.0940 + 0.1670 = 0.2610$$

In column IV., $v - b$, is calculated from the equation

$$\pi = \pi_0 e^{c'/T^v} = \frac{RT}{v - b}$$

$$\text{or} \quad v - b = \frac{B'T}{e^{c'/T^v}}$$

$$\text{where} \quad B' = \frac{R}{\pi_0} = 0.001677$$

$$\text{and} \quad c' = 428.5.$$

As b has been considered a constant, which is probably true only to a first approximation, the agreement is satisfactory.

The Effective Molecular Weight in a Liquid.

The view has been taken that a certain number of molecules tend, under the ordinary van der Waals' forces, to combine momentarily. These molecules would increase the average effective molecular weight. The forces which control the number of temporarily combined molecules are the forces which ultimately cause the liquid to solidify. Combination of this sort will, therefore, occur in all liquids. If in addition to the ordinary van der Waals' forces, there are also polar forces present, association will be of a more extensive and permanent nature. The van der Waals' forces in most liquids being very similar, it would be impossible to detect this type of association by many physical methods, because it is the normal and inevitable condition of a liquid. The divergences of liquids, however, from generalised laws are probably due to varying degrees of association.

As with the internal pressure, we should expect the effective molecular weight to be equal to the true molecular weight multiplied by an exponential term, following Maxwell's law, or if M_0 is the true molecular weight, the effective molecular weight should be $M_0 e^{c''/T^v}$, where c'' is a constant. In spite of the above statement, a liquid would act in most physical changes as though its molecular weight were M_0 , because in

⁴ *Trans. Roy. Soc., A*, 1894.

any interchange of molecules, those temporarily in association would automatically be excluded. Under great external pressure, the effective molecular weight would be still further increased, accounting in part for the great increase in viscosity of liquids under pressure. In general we would expect c'' to be less than c' , because two molecules would need to be in much closer association to move as one, than they would need to be to exert an internal cohesion greater than the average.

The Viscosity of a Liquid.

We now replace the quantity $M_0\alpha$ in the equation $\eta = \frac{KM_0\alpha}{v-b}$ by the quantity M_0e^{c''/T_0} so that

$$\eta = \frac{KM_0e^{c''/T_0}}{v-b} \quad (2)$$

Substituting for $v-b$, the quantity $\frac{RT}{\pi_0 e^{c'/T_0}}$

from equation (1) we have,

$$\begin{aligned} \eta &= \frac{KM_0 \cdot \pi_0 \cdot e^{c'/T_0} \cdot e^{c''/T_0}}{RT} \\ &= \frac{Be^{c'/T_0}}{T} \end{aligned} \quad (3)$$

where

$$B = \frac{KM_0\pi_0}{R} \text{ and } c = c' + c''.$$

This is very similar to Andrade's equation

$$\eta e^{c/T} = Be^{c'/T}$$

and can be shown to give a similar agreement between observed and calculated values.

$$\text{The equation } \eta = \frac{KM_0 \cdot e^{c''/T_0} \cdot \pi_0 e^{c'/T_0}}{RT}$$

means that the viscosity of a liquid is directly proportional to its internal pressure and to the effective molecular weight and inversely proportional to the absolute temperature.

It will be noted that whereas each of the equations $\eta = \frac{KM_0e^{c''/T_0}}{v-b}$ and $\pi_0 e^{c'/T_0} = \frac{RT}{v-b}$ contains three unknowns, by eliminating $v-b$ we get $\eta = \frac{Be^{c'/T_0}}{T}$ containing two unknowns.

The application of the equation

$$\eta = \frac{KM_0e^{c''/T_0}}{v-b}$$

to octane will now be given. The value of the free space, $v-b$, is the same as that used for the change of volume with temperature namely 0.0940.

In Table II., column II., gives the observed values of the viscosity taken from Thorpe and Rodger.⁴ Column III. gives the values of the viscosity calculated from equation (2) with $KM_0 = 0.034037$, $c'' = 134.5$

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and $v - b = 0.0940$. It will be seen that the agreement between the observed and calculated values is within the experimental error.

TABLE II.—OCTANE.

I. Temp. °C.	II. %obs.	III. %calc.
0	0.00703	0.00703
10	0.006125	0.00614
20	0.00538	0.00537
30	0.004785	0.00477
40	0.00428	0.00427
50	0.003855	0.003852
60	0.003495	0.003495
70	0.00318	0.00318
80	0.002905	0.002903
90	0.00266	0.00266
100	0.002445	0.002445
110	0.002255	0.002250
120	0.002075	0.002074

TABLE III.

Temp. °C.	%obs.	%calc.	Percentage Error.
0	0.00703	0.00697	— 0.9
10	0.006125	0.00609	— 0.5
20	0.00538	0.00538	0.0
30	0.004785	0.004785	0.0
40	0.00428	0.00428	0.0
50	0.003855	0.003856	0.0
60	0.003495	0.003490	— 0.1
70	0.00318	0.003174	— 0.2
80	0.002905	0.002897	— 0.3
90	0.00266	0.00266	0.0
100	0.002445	0.002445	0.0
110	0.002255	0.002255	0.0
120	0.002075	0.002085	+ 0.5

In applying the equation $\eta = \frac{Be^{c/T}}{T}$ to the same liquid, c should of course be equal to $c' + c''$. A separate solution has been made for each table so that whereas the value taken for c in Table III. is 565.5,

$$c' + c'' = 428.5 + 134.5 = 563.0$$

The difference, therefore, is very small.

In Table III. $B = 0.2392$ and $c = 565.5$.

Comparison with Andrade's figures for octane (*loc. cit.*, p. 710) shows that the above agreement is similar to that obtained from his equation. Application to other liquids reveals a similar agreement.

As Andrade has discussed extensively the application of an equation of this type it is unnecessary to give further illustrations. The meaning of the constants in both cases must be similar.

I wish to thank Dr. C. Coleridge Faur, F.R.S., for encouragement in this work.

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ON THE DECOMPOSITION OF DIAZO-ACETIC ESTER CATALYSED BY PROTONS AND DEUTONS.

By PH. GROSS, H. STEINER AND F. KRAUSS.

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In this paper we record experiments on the decomposition of diazo-acetic ester in mixtures of heavy and light water when catalysed by protons and deutons, which were carried out in order to gain a better insight into the mechanism of such reactions. They form part of our investigation into the connection between kinetics and thermodynamics in such mixtures reported in the succeeding two papers.

The decomposition of diazo-acetic ester is well suited for such purposes both for experimental and theoretical reasons. Firstly, the measurement of the reaction rate can be carried out easily on a micro-scale by determining the volume of nitrogen produced in the course of the reaction $\text{N}_2\text{CH}-\text{COOC}_2\text{H}_5 + \text{H}_2\text{O} = \text{HOCH}_2-\text{COOC}_2\text{H}_5 + \text{N}_2$. Secondly, this reaction cannot, so far as we know, be taken as an example of generalised acid catalysis.¹ In order to avoid complications we used picric acid to acidify the solutions.

I. Experimental.

(a) Materials.

The ester used was purified² and redistilled in vacuo several times. The solutions of picric acid (Merck p.a.) were prepared by mixing measured amounts of a standard solution of picric acid in D_2O with measured amounts of a 0.01 *N* aqueous (H_2O) solution of picric acid. The standard solution in D_2O was prepared by weighing out picric acid into D_2O , using a micro-balance. The acidity and the total amount of deuterium present in the mixtures were computed from the concentrations and amounts of the constituents.

(b) Apparatus and Experimental Procedure.

The reaction vessel * was a bulb of about 1 c.c. capacity attached to the other parts of the apparatus by two ground joints. To avoid supersaturation a stream of the air present in the apparatus could be circulated through the solution. Preliminary experiments in a Jena glass vessel yielded values markedly lower than that extrapolated for 0° C. from values ascertained in older macroscopic measurements. With a vessel of quartz-glass these differences almost disappeared. The lower reaction rate with the glass vessel may have been due to adsorption of part of the picric acid at the glass surface.

The volume of the nitrogen evolved was measured at constant pressure.

¹ J. N. Brönsted, *Chem. Rev.*, 1928, 5, 251.

² W. Fraenkel, *Z. physik. Chem.*, 1907, 60, 202.

* A more detailed description of the apparatus used in these experiments will be given later in *Mikrochemie*.

In each experiment there was placed in the reaction vessel first 5 c.mm. of ester and then 0.37 c.c. of picric acid solution, which corresponds to a dilution of the ester to 1.3 per cent. strength. As thermostat we employed a Dewar flask with ice water agitated by a current of air.

After six to ten readings had been made the reaction vessel was immersed in water at a temperature of 30–40° C., for the purpose of completely decomposing the ester. After the lapse of half an hour the final volume was read off with the reaction vessel in an ice bath.

II. Results.

The values of $\ln \frac{a}{a-y}$ were plotted as a function of the time t , y denoting the reading at time t , a the initial reading. The points fit very well to a straight line. The velocity constants were obtained by dividing the slope of these lines by the picric acid concentration. In Table I. all the values obtained are given:—

TABLE I.—THE DECOMPOSITION RATE OF DIAZO-ACETIC ESTER AT 0° C. AS A FUNCTION OF THE D₂O CONTENT OF THE SOLVENT WATER.

x .	$P \cdot 10^4$.	$\frac{dS}{dt} \cdot \frac{1}{P \cdot S}$.	$\xi(x)$.	$Q(x)$.
0.000	—	2.40 †	1.00	1.00
0.243	0.872	2.87	1.19	0.81
0.365	0.850	3.25	1.35	0.70
0.487	0.735	3.72	1.55	0.60
0.733	0.695	4.55	1.89	0.473
0.977	0.454	6.10	2.55	0.337
0.987	0.920	6.33	2.64	0.327
1.000	—	6.37 ‡	2.70	0.317

* t in minutes. † Average value. ‡ Extrapolated.

x = Analytic mole fraction of D₂O.

P = Analytic concentration of picric acid in mole/litre.

$$\xi(x) = \frac{\frac{dS}{dt} \cdot K_f}{P \cdot S \cdot k_i}$$

energy of the D substrate bond; but one has to expect that the activation does not take place in this bond otherwise the two effects would cancel each other. In both the two hitherto known cases the rates of reaction are about doubled, so that the increase found in the present instance represents the highest yet known. In this connection we want to emphasise that in the present case, as already mentioned, most certainly no generalised acid catalysis occurs. In the light of thermodynamic considerations suggested by this investigation and that of cane sugar inversion a somewhat more detailed analysis is given later.*

* E. A. Moelwyn-Hughes and K. F. Ponhoefier, *Naturwiss.*, 1934, 22, 174; K. Schwarz, *Anzeiger Akad. Wiss. Wien.*, 1934, 26, IV.

* W. F. K. Wynne-Jones, *J. Chem. Physics*, 1934, 2, 384; O. Halpern, *J. Chem. Physics*, 1935, 3, 456. See also E. A. Moelwyn-Hughes, *Z. physik. Chem.*, (B), 1934, 26, 279; this author, however, assumes formation of a complex consisting of the substrate and a hydrated H (D) ion.

* This number, Gross, Steiner and Suess, p. 883.

The hydrolysis of diazo-acetic ester thus proceeds in pure heavy water roughly three times as rapidly as in pure light water, the increase in rate being not linear. The increase in the rate of such hydrolytic reactions in heavy water is known³ and has already been discussed.⁴ It has been attributed to an increase in the concentration of a reacting complex consisting of substrate and either H or D ion. This increase is due to the smaller zero point

Summary.

The decomposition rate of diazo-acetic ester in mixtures of light and heavy water catalysed by H and D ions at 0° C. increases with the D content of the solvent and is in pure heavy water about three times as high as in pure light water. The increase is far from being a linear function of the analytical D content.

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ON THE DISTRIBUTION OF PICRIC ACID BETWEEN BENZENE AND MIXTURES OF LIGHT AND HEAVY WATER.

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In order to investigate whether inherent relations exist between the rate of reactions in water with changing D₂O content and the conditions governing the equilibrium in such mixtures we measured the distribution of picric acid between water of various compositions and benzene. Picric acid is especially well suited for the purposes of this investigation, as in dilute aqueous solutions the partition ratio does not differ much from unity and the acid can be taken as being perfectly dissociated.

I. Experimental.

(a) Materials.

The picric acid was recrystallised several times and had been proved to be optically pure in previous occasions.¹ The benzene was free from thiophene and washed with alkaline solution and with water. One part of the deuterium oxide was prepared by electrolysis and then redistilled in a high vacuum, the rest was a commercial product of neutral reaction against phenolphthalein. Conductivity water was used for control experiments in pure light water.

(b) Method of Analysis.

For all our experiments we prepared a 0.02979 molal standard solution by weighing out picric acid into benzene. The concentration was checked several times. The concentration of the approximately N/10 alkali solution was determined by titration with aqueous solutions of picric acid prepared by direct weighing. As indicator we used phenolphthalein and a standard solution as a basis for colour comparison. By carrying out the titrations in the actual experiments in the same manner, minor systematic errors due possibly to the fact that not quite the right colour was taken as end-point and that the amount of carbon dioxide present in the solution was disregarded are cancelled. For measuring the volume of the solutions, carefully calibrated micro-pipettes of 1 c.c. and 0.5 c.c. capacity were used and for titration a micro-burette² of 200 c.mm. capacity permitting readings to within 0.5 c.mm.

¹ Ph. Gross, A. Jamölk and F. Patat, *Sitz. Ber. Akad. Wiss., Wien, IIb*, 1933, 142, 327; *Monatsh. Chem.*, 1933, 63, 117.

² K. Schwarz, *Mikrochemie*, 1933, 13, 1, and 1935, 18, 309.

The D_2O percentage of the water was determined by density measurements, using the above described 1 c.c. pipette as a pycnometer, invariably filled, in a thermostat at 18° C.

(c) Experimental Procedure.

All experiments were carried out in a thermostat at $18.00 \pm 0.005^\circ$ C. One c.c. of water was shaken with 1 c.c. of the standard solution of picric acid in benzene in a sealed-up tube of Jena glass for half an hour. After the two layers had been allowed to separate and become clear for again half an hour 0.5 c.c. of each of the phases were withdrawn with the pipette and titrated.

II. Results.

The results of the measurements are given in Table II. The total amount of picric acid should naturally equal the sum of the amounts found in both phases. The sum found is given in Table II. column Σ . The differ-

TABLE II.—DISTRIBUTION COEFFICIENT OF PICRIC ACID BETWEEN BENZENE AND WATER AT 18° C. AS A FUNCTION OF THE D_2O CONTENT OF THE SOLVENT WATER.

D_{18}^{18}	x	$c_b \cdot 10^3$	$c_w \cdot 10^3$	$\Sigma \cdot 10^3$	K	$\eta(x)$	$Q(x)$
1.0000	0.0000	—	—	—	234.8 *	1.00	1.000
1.0023	0.0217	1.982	1.006	2.987	246.8	1.05	0.957
1.0274	0.2556	2.122	0.889	3.002	333.5	1.42	0.758
1.0469	0.426	2.218	0.815	3.115	407.7	1.75	0.650
1.0520	0.482	2.260	0.797	3.057	437.1	1.86	0.613
1.0585	0.543	2.245	0.740	2.983	500.0	2.13	0.544
1.0822	0.765	2.395	0.690	3.082	609.0	2.59	0.473
1.0942	0.874	2.360	0.615	2.971	746.2	3.18	0.395
1.1065	0.991	2.450	0.557	3.006	938.2	3.99	0.319
—	1.000	—	—	—	—	4.05 †	0.317

* Average value.

† Extrapolated.

D_{18}^{18} = Density at 18° C. referred to water at 18° C.

x = Analytical mole fraction of D_2O .

c_b = Concentration of picric acid in the benzene phase in mole/litre.

c_w = Concentration of picric acid in the aqueous phase in mole/litre.

Σ = Sum of the amount of picric acid found in both phases.

K = Thermodynamic distribution constant = $\frac{c_b}{c_w \cdot \gamma^2}$.

γ = Interionic activity coefficient.

$\eta(x)$ = Ratio of K to the respective constant for pure light water.

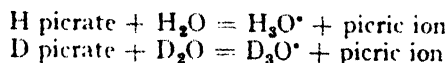
ence between the amount of picric acid actually used (in all cases 0.02963) and the values of Σ averages about 1.8 per cent. The thermodynamic constant of distribution was computed from the concentration of picric acid in water (c_w) and in benzene (c_b) with the help of the activity coefficient of picric acid determined with the aid of the well-known Debye-Hückel formula. According to this formula we have at 18° C.: $\log \gamma^2 = \sqrt{c_w}$. The value given in the table for pure light water is a mean value of 10 independent measurements all carried out on a micro scale. The average error in any single measurement was 1.4 per cent. The difference between the value obtained in these blank experiments and that calculated ⁷

⁷ Ph. Gross and O. Halpern, *Physik. Z.*, 1924, 25, 393.

from the results of the experiments made by Rothmund and Drucker⁸ (showing an error of 1.4 per cent. in K and of 0.6 per cent. in Σ) is about 4.3 per cent. In our opinion this minor difference is systematic and may perhaps be due to the fact that our experiments were carried out on a micro-scale. It should be noted that all the Σ values are greater than the amount of picric acid actually used and that these differences are of the same order of magnitude as the differences between the present value and the value found by Rothmund and Drucker. Therefore the ratio K/K_0 may have a small error.

III. Discussion and Theory.

The change which the distribution of picric acid undergoes when pure heavy water is substituted for pure light water as solvent, is attributable to a change in dissociation energy. This change is due to the fact that the zero point energy of the H- and D-linkage in the initial and end states of the reactions



differ from each other. We believe it to be a justifiable assumption that the solubility of the undissociated molecules does not change. This diminution of the dissociation constant has been observed already in the case of water and of acetic acid and is to be expected in view of Halpern's theoretical treatment⁹ of this question in all cases in which the dissociation constant (when expressed in moles/litre) is less than approximately the number of water molecules in a litre.

The following treatment will be an aid to understanding the dependence of the distribution coefficient on the composition of water.

If h and d denote the activities of protons and deuterons respectively, we have, according to the reaction $2\text{H}^+ + \text{D}_2\text{O} = 2\text{D}^+ + \text{H}_2\text{O}$:

$$\frac{h}{d} = \frac{1}{q} \sqrt{\frac{a_{\text{H}_2\text{O}}}{a_{\text{D}_2\text{O}}}} \quad (1.1)$$

In this $a_{\text{H}_2\text{O}}$ and $a_{\text{D}_2\text{O}}$ denote the activities of H_2O and D_2O respectively, and q is a constant. We now limit ourselves to solutions which are so dilute that the mole fraction of the water molecules linked to H- or D-ions (H_3O^+ , H_2DO^+ , HD_2O^+ , D_3O^+) is small compared with the mole fraction of the corresponding free water molecules (H_2O , HDO , D_2O). Then the proton activity is nothing but the product of the following two factors: (a) picric ion activity and (b) a function of the D_2O content. The activity of picric ions equals the product of the analytical concentration of picric acid P and the interionic activity coefficient γ , because the acid can be regarded as perfectly dissociated. Thus

$$h = P \cdot \frac{1}{Q(x)} \cdot \phi(x) \cdot \gamma \quad (1.2)$$

and similarly

$$d = P \cdot \frac{q}{Q(x)} \cdot \psi(x) \cdot \gamma \quad (1.3)$$

if x denotes the analytical mole fraction of D_2O , and $\phi(x)$, $\psi(x)$ and $Q(x)$ denote different functions of x . A comparison of (1.2) and (1.3) with

⁸ V. Rothmund and C. Drucker, *Z. physik. Chem.*, 1903, **46**, 827.

⁹ O. Halpern, *J. Chem. Physics.*, 1935, **3**, 450.

(1.1) shows that $\phi(x)$ is proportional to the square root of the H_2O activity, $\psi(x)$ is proportional to the square root of the D_2O activity. The proportion constant is taken to be unity. According to the usual practice we define the proton activity in pure light water at the reference temperature as $h = P \cdot \gamma$, and similarly the deutron activity in pure heavy water as $d = P \cdot \gamma$. Then we have

$$\begin{aligned} Q(0) &= 1. & \phi(0) &= 1. \\ Q(1) &= q. & \psi(1) &= 1. \end{aligned}$$

The value of the equilibrium constant

$$L = \frac{a_{HDO}^2}{a_{H_2O} \cdot a_{D_2O}} \quad . \quad . \quad . \quad . \quad (2)$$

is essentially dependent on the difference between the zero point energies.¹⁰ The heat of reaction experimentally found¹¹ gives a value of $L = 3.97$. If we therefore assume that L is about 4 and furthermore that the association of the water molecules does not change the equilibrium we can take the activities to be identical with the mole fractions of the individual types of water molecules. Thus

$$a_{H_2O} = (1 - x)^2, \quad . \quad . \quad . \quad . \quad (3.1)$$

$$a_{HDO} = 2x(1 - x), \quad . \quad . \quad . \quad . \quad (3.2)$$

$$a_{D_2O} = x^2. \quad . \quad . \quad . \quad . \quad (3.3)$$

Thus we have instead of (1.1), (1.2) and (1.3) :

$$\frac{h}{d} = \frac{1}{q} \cdot \frac{1 - x}{x}, \quad . \quad . \quad . \quad . \quad (1.1')$$

$$h = P \cdot \frac{1}{Q(x)} \cdot (1 - x) \cdot \gamma, \quad . \quad . \quad . \quad . \quad (1.2')$$

$$d = P \cdot \frac{q}{Q(x)} \cdot x \cdot \gamma. \quad . \quad . \quad . \quad . \quad (1.3')$$

For the distribution of picric acid between benzene and pure light water the following relation holds :

$$h \cdot P \cdot \gamma = \frac{c_l}{K_l} \quad . \quad . \quad . \quad . \quad (4.1)$$

and similarly for pure heavy water :

$$d \cdot P \cdot \gamma = \frac{c_h}{K_h} \quad . \quad . \quad . \quad . \quad (4.2)$$

Here K_l and K_h denote the distribution constants of picric acid between benzene and pure light or pure heavy water respectively, c_l and c_h the concentration of light and heavy picric acid, respectively, in benzene. From (4.1) and (4.2) we obtain the dependency of the distribution constant on the composition of the water. The ratio of this constant to the constant in pure light water is therefore

$$\eta(x) = \frac{c_h}{\gamma^2 P^2 K_l} = \frac{1}{Q(x)} [1 - x(1 - q \cdot \eta(1))]; \quad c_b = c_l + c_h. \quad (5)$$

¹⁰ B. Topley and H. Eyring, *J. Chem. Physics*, 1934, **2**, 217.

¹¹ E. Doehlemann and E. Lange, *Z. Elektrochem.*, 1935, **41**, 539.

The value of q can be computed from ¹²

$$q = \frac{1}{M} \sqrt{\frac{L}{N}} \exp. \frac{(\epsilon_H - \epsilon_D)F}{RT},$$

therein $M = \frac{[H_2] \cdot a_{HDO}}{[HD] \cdot a_{H_2O}} = 3.04$ and $N = \frac{[HD]^2}{[H_2][D_2]} = 3.26$ denote

equilibrium constants and $\epsilon_H - \epsilon_D = 3.4 \times 10^{-3}$ Volt, the normal potential difference,¹³ the numerical values holding at room temperature (21° C.). Not even a considerable error in this difference would change the value of q appreciably.

We calculated a series of points of the function $Q(x)$ governing the equilibrium of the different water ions from our distribution measurements for the corresponding values of x with the help of the above given value of q and plotted them against x in a graph reproduced in the next paper (Gross, Steiner and Suess (p. 886), where there also is given another method of calculating the function $Q(x)$). For this reason and for the sake of brevity a more detailed combined discussion has been reserved for this later paper.

Summary.

The distribution of picric acid between benzene and mixtures of light and heavy water at 18° C. has been measured. The distribution coefficient increases with the D₂O content but not linearly. The value of the distribution constant in pure heavy water is about four times as great as in pure light water. This effect is due to the differences between the zero point energies in the various D- and H-linkages. The dependence of the distribution constant on the composition of the water is treated from the standpoint of thermodynamics.

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¹² See O. Halpern and Ph. Gross, *J. Chem. Physics*, 1935, 3, 454, equation (11).

¹³ E. Abel, E. Bratu and O. Redlich, *Z. physik. Chem. (A)*, 1935, 173, 360.

THE INVERSION OF CANE SUGAR IN MIXTURES OF LIGHT AND HEAVY WATER.

BY PH. GROSS, H. STEINER AND H. SUESS.

Received 13th March, 1936.

This paper deals with cane sugar inversion in mixtures of light and heavy water. After an account of the experiments made we pass on to an attempt to carry out as general as possible an analysis of the equilibria in which the ions of "water" participate. On the strength of this analysis it becomes possible, in conjunction with the experiments carried out, to draw conclusions as to the mechanism of reactions catalysed by hydrogen ions.

I. Experimental.

All solutions were prepared in the following manner: To 0.2 g. of water, the isotopic composition of which was determined by density measurement, we added, with the aid of a micro-pipette, a measured amount of approximately 7 *N* sulphuric acid of known concentration. To the approximately 0.3 *N* sulphuric acid thus obtained we added an accurately weighed out quantity of cane sugar (approximately 10 per cent. by weight). In experiment 6 we employed the corresponding quantity of titrated concentrated sulphuric acid instead of the 7 *N* acid. In ascertaining the total D content, allowance was made for the dilution due to the addition of sulphuric acid and sugar. For measurement of the optical rotation we employed a polarimeter capable of reading to within 0.01° and a micro-tube of 5 cm. length and 1 mm. diameter. The source of light was a sodium discharge lamp of high brilliancy. Each polarimeter reading represents the average of three independent settings. The experiments were carried out in a thermostat at $25 \pm 0.05^\circ \text{C.}$, the micro-polarimeter tube being removed just for the short time of readings. As the tube was not equipped with a jacket the room was heated to 25°C. At the start, readings were taken every 20 minutes and were continued until no alteration in the rotation could be detected for several hours on end. From the last of the values obtained we deduced the initial concentration.

The constants were obtained in the usual graphical manner, the single points fitting very well to a straight line.

II. Results.

Table III. gives the results of all experiments and the values for pure heavy water extrapolated therefrom.

TABLE III.—THE INVERSION RATE OF CANE SUGAR AT 25°C. AS A FUNCTION OF THE D_2O CONTENT OF THE SOLVENT WATER.

x .	P .	$\frac{dS}{dt} \cdot \frac{10^3}{P \cdot S}^*$	$\zeta(x)$.	$Q'(x)$.
0.000	—	5.15 †	1.00	1.000
0.225	0.262	5.72	1.11	0.831
0.447	0.333	6.24	1.21	0.700
0.666	0.280	7.07	1.37	0.563
0.842	0.287	8.39	1.63	0.437
0.984	0.213	10.37	2.01	0.330
1.000	—	—	2.05 ‡	0.317

* t in minutes.

† Average value.

‡ Extrapolated.

x = Analytic mole fraction of D_2O .

P = Analytic concentration of sulphuric acid in aequiv./litre.

$$\zeta(x) = \frac{\frac{dS}{dt} \cdot K_1'}{P \cdot S \cdot k_1'}$$

If the values for $\frac{1}{\zeta(x)}$ be plotted against x they will be found to lie on a continuous curve the form of which permits extrapolation of the value $\zeta(1) = 2.05$ for pure heavy water without danger of a serious error. Between this value and that arrived at by Moelwyn-Hughes¹⁴ there is a difference which is obviously greater than the respective experimental

¹⁴ E. A. Moelwyn-Hughes, *Z. physik. Chem.*, 1934, **26B**, 278.

errors. As yet we have had no opportunity of going into the question of this discrepancy. It may possibly be due to the difference in concentration between the catalysts used.

III. Theoretical Discussion.

(a) Preliminary Remarks.

The alteration in the rate of reactions catalysed by hydrogen ions on passing from light to heavy water as solvent has been attributed to the difference between the concentrations of the reacting complex. This complex consists of the substrate to which there is linked in the one case an H ion, in the other case a D ion. Proceeding from this assumption, the dependence of the reaction rate on the D_2O content of the solvent is completely described by the thermodynamic conditions, provided the following pre-suppositions are in accordance with fact:

1. That the decomposition constant is unaffected by the medium, *i.e.*, that the reaction with the water takes place, either after each activation in the narrower sense, or just as readily with H_2O as with D_2O (the contribution of the zero point energy of the water molecule non-existent or negligible or cancelled).

2. That the concentration of the complex is invariably the equilibrium concentration, *i.e.* the rate of formation of the complex is great in comparison with the reaction rate.

Assuming these pre-suppositions to be justified the following equation holds for the reaction rate:

$$-\frac{dS}{dt} = k_l \frac{h \cdot S}{\gamma \cdot K_l'} + k_h \frac{d \cdot S}{\gamma \cdot K_h'} \quad (6)$$

We now use the same notation as before: h and d for the activities of proton and deuteron respectively, γ for the interionic activity coefficient. In addition k_l and k_h stand for the reaction constants in pure light and pure heavy water, and K_l' and K_h' for the dissociation constants of the reacting complex; S denotes the concentration of the substrate. From this equation we obtain (with the help¹⁵ of equations (1.2') and (1.3')) for the ratio between the reaction constant for any desired composition of water and the reaction constant for pure light water:

$$\zeta(x) = \frac{\frac{ds}{dt} \cdot K_l'}{P \cdot S \cdot k} = \frac{1}{Q(x)} \cdot 1 - x(1 - q \cdot \zeta(1)) \quad \zeta(1) = \frac{k_h}{k_l} \cdot \frac{K_l'}{K_h'} \quad (7)$$

In perfect analogy with the thermodynamics of picric acid distribution the function $Q(x)$ can be computed from the function $\zeta(x)$. We calculated the values for the function $Q(x)$ on the one hand from the ascertained values for picric acid distribution, and on the other hand from measurements of the reaction rates of diazo-acetic ester decomposition and of cane sugar inversion, and plotted them in the diagram (Fig. 1) against the D_2O content of the solvent. All the experiments ought of course to have been carried out at the same temperature. Since this, however, was not possible for experimental reasons, the temperature differences are for the time being neglected on the assumption that the temperature coefficients of the constants concerned are so small that

¹⁵ We refer to equations of the preceding paper by number only.

the deviation within the range of temperature involved is of subsidiary significance.

It will be seen that the course of the function $Q(x)$ obtained in the case of the decomposition of diazo-acetic ester is the same as that obtained in the case of picric acid distribution. This agreement is hardly affected by the numerical value of the constant q . We conclude from this agreement that, in the case of the ester decomposition, the above-mentioned pre-suppositions are very fairly true so that the analogy emphasised by Halpern¹⁶ is indeed perfect.

The same agreement would of course follow from the assumption of a bimolecular collision mechanism in which the reaction rate constants

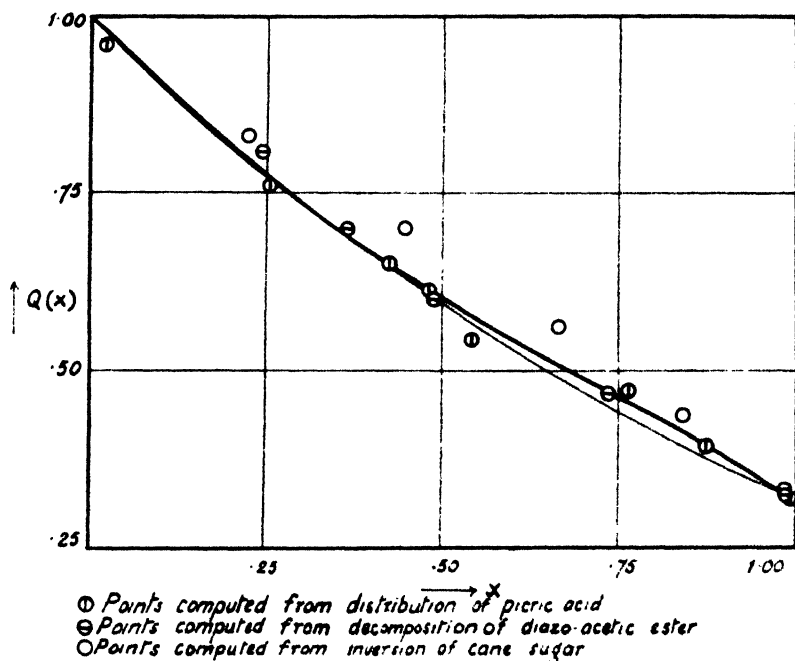


FIG. 1.

are inverse proportional to the equilibrium constants. This, however, is hardly probable¹⁷ and merely *ad hoc*.

(b) Calculation of the Ionic Equilibria in Water.

Before discussing the deviations occurring in cane sugar inversion we will give a more detailed statement of the physical significance of the function $Q(x)$, the more general bearing of which proceeds clearly from the agreement found in the two cases just mentioned. For this purpose it is assumed that the ions H_3O^+ , H_2DO^+ , HD_2O^+ and D_3O^+ are actually present.

Then, on the truly very general assumptions made in the preceding paper, the most general form of the equilibrium conditions is :

¹⁶ O. Halpern, *J. Chem. Physics.*, 1935, **3**, 456.

¹⁷ See J. N. Brønsted, *Chem. Rev.*, 1928, **5**, 318.

$$\frac{[H_2O'] \cdot \gamma}{h \cdot a_{H_2O}} = 1 \quad (8.1) \quad \frac{[D_2O'] \cdot \gamma}{d \cdot a_{D_2O}} = 1 \quad (9.1)$$

$$\frac{[H_2DO'] \cdot \gamma}{h \cdot a_{HDO}} = \frac{3}{2} r_2 \quad (8.2) \quad \frac{[HD_2O'] \cdot \gamma}{d \cdot a_{HDO}} = \frac{3}{2} s_2 \quad (9.2)$$

$$\frac{[HD_2O'] \cdot \gamma}{h \cdot a_{D_2O}} = 3r_1 \quad (8.3) \quad \frac{[H_2DO'] \cdot \gamma}{d \cdot a_{H_2O}} = 3s_1 \quad (9.3)$$

and

$$\frac{h \cdot oh}{a_{H_2O}} = k_{11} \quad (10.1) \quad \frac{d \cdot oh}{a_{HDO}} = k_{21} = \frac{k_{11}}{2} \frac{r_2}{s_1} \quad (10.3)$$

$$\frac{h \cdot od}{a_{HDO}} = k_{12} = \frac{k_{22}}{2} \frac{s_2}{r_1} \quad (10.2) \quad \frac{d \cdot od}{a_{D_2O}} = k_{22} \quad (10.4)$$

if we denote the mole fractions by the respective chemical symbols in brackets, the activities of the hydroxyl ions by *oh* and *od*, and if the *r*, *s* and *k* are constants.

In this connexion the same assumption is made as to the units of the activities as was made in the previous paper, which of course does not detract from the universal character of these equations.

By comparing (9.3)/(8.2) and (9.2)/(8.3) with (1.1) and (2) we find

$$q = \frac{2}{\sqrt{L}} \cdot \frac{r_2}{s_1} = \frac{\sqrt{L}}{2} \cdot \frac{r_1}{s_2}$$

And if we assume

$$L = 4 \quad (11.1)$$

it follows that

$$q = \frac{r_2}{s_1} = \frac{r_1}{s_2} \quad (11.2)$$

Since account has been taken of the statistical weights by introducing the numerical factors¹⁸ it would appear obvious to assume that the constants *r* and *s* are equal to unity. This, however, would lead to consequences in contradiction with facts, as, e.g., a glance at (11.2) shows. On this assumption the cane sugar inversion also would be linearly dependent on concentration. The deviations from the linear and considerations connected with this train of thought (see equations 10) led us to conclude that the dissociation constants of heavy and light water are unequal.¹⁹ The assumption *r* = *s* = 1 is therefore mistaken. It is only admissible to assume that the constants *r* and *s* are of the order of magnitude of unity.

Proceeding from the condition of electro-neutrality we get with the aid of the equations (1.1'), (1.2'), (3.1) – (3.3), (8.1) – (8.3) and (9.1)

$$Q(x) = 1 - 3x(1 - r_2) + 3x^2(1 - 2r_2 + r_1) - x^3 \left(1 - 3r_2 + 3r_1 - \frac{r_2}{s_1} \right) \quad (12)$$

If we choose *r*₁ = 0.50 and *r*₂ = 0.64 we obtain the curve which is shown in Fig. 1 as a thick line and which fits best the ascertained values. For *s*₁ and *s*₂ we thus obtain with the help of *q* = 0.317 the values *s*₁ = 2.02 and *s*₂ = 1.59.

It would naturally appear desirable to obtain, in addition to purely experimental data, theoretical indications for determining the constants,

¹⁸ R. Wegscheider, *Monatsh f. Chem.*, 1895, 16, 153.

¹⁹ See Ph. Gross, H. Suess and H. Steiner, *Naturwiss.*, 1934, 22, 662.

especially seeing that the experimental determination of the constants r is based on measurements carried out on a micro-scale and therefore not very accurate. The most plausible assumption for this purpose, having regard only to the different symmetries of the ions H_3O^+ , H_2DO^+ and HD_2O^+ , would be that $r_2 = \sqrt{r_1}$ and $s_2 = \sqrt{s_1}$. This assumption simplifies the function $Q(x)$ to

$$Q(x) = [1 - x(1 - \sqrt{r_1})]^3 \quad \sqrt{r_1} = \sqrt[3]{q}.$$

The curve representing this function is shown as a thin line in Fig. 1. It will be seen that the two curves do not differ much one from the other.

(c) On the Mechanism of the Inversion of Cane Sugar and Similar Reactions.

In the case of cane sugar inversion there occur systematic deviations which are small but obviously outside the limits of experimental error. These may be due to the fact that we used sulphuric acid as catalyst and regarded it as being completely dissociated. If this brings about too great an error the change in the degree of dissociation of HSO_4^- ions with changing D_2O content should have been allowed for. Since the value of (1) has been found¹⁴ to be independent of the catalysing acid (DCl or D_2SO_4), albeit with a smaller concentration, it seems that this effect is not of great influence.

Further, it might be assumed that we are here concerned with a quantum mechanical resonance effect, similar to that in the case of the conductivity of hydrogen ions in mixtures of heavy and light water, which effect would be at its weakest in mixtures of approximately equal parts.* This possibility cannot, it is true, be precluded with certainty, but we are not entitled to draw any conclusions in favour of such an effect from the mere fact that the ascertained values deviate most markedly just in mixtures of equal parts, since, by definition, there must be agreement in the endpoints.

Finally we have to discuss the consequences when one of the above mentioned pre-suppositions is not justified. This discussion is of more general theoretical importance.

If the calculation is carried out on the assumption that the true activation energy of the reacting partners is different owing to the difference of the zero point energies, the function $Q(x)$ will be found to be

$$Q(x) = \frac{1}{(x)} [1 - x(1 - q \cdot (1))] \cdot [1 - x(1 \pm b)] \quad (14)$$

b denoting the relative difference between the true velocity constants. If one inserts for b a value of the order of magnitude of that found experimentally in the case of enzymatic cane sugar inversion,²⁰ i.e. $\pm 1/4$ the deviations remain systematic and approximately of the same magnitude as before.

* This is actually the fact in the case of H and D ion mobility. The conductivity of a strong acid is not a linear function of the D_2O content. If the relative deviations from the straight line passing through the end points be plotted against the D_2O content in accordance with the experiments carried out by W. N. Baker and V. K. la Mer (*J. Chem. Physics.*, 1935, 3, 406) (at 26° C.) a nearly parabolic curve results with the maximum at about $x = 0.5$. If the same is done in accordance with our own experiments (*Sitzber. Akad. Wiss., Wien*, 11 b, 1935, 144, 243; *Monatsh. Chem.*, 1935, 66, 111) carried out on a micro scale and at a different temperature (18° C.) practically the same curve is obtained.

²⁰ E. W. R. Steacie, *Z. physik. Chem. (B)*, 1934, 27, 6.

If the other pre-supposition is not in accordance with fact *the concentration of the complex actually obtaining is not invariably the equilibrium concentration, and the reaction rate is therefore not governed by the equilibrium concentration. This will be the case if generalised acid catalysis occurs.*²¹ Moreover agreement with thermodynamics is not to be expected in the second case treated by Halpern.¹⁶ In this case the complex concerned (the concentration of which is very small), behaves like an extremely strong acid. What would be expected is generalised acid catalysis, the formation of the complex being the rate determining step. A lessening of the reaction rate has, indeed, been found in the case of mutarotation of glucose²² which is a thoroughly investigated example of generalised acid catalysis.²³

An indication that in the special case of cane sugar inversion, generalised acid catalysis also plays a part, and that therefore the second pre-supposition is not quite justified, is supplied by experiments of Hantzsch and Weissberger²⁴ which have been discussed by Hammet and Paul.²⁵

In any event, the deviations are of minor importance and the experiments corroborate the view that the increase in reaction rate is due to an increase in the concentration of the reacting complex, and that on this effect there is superposed a further effect which may possibly be closely connected with other irregularities met with in cane sugar inversion.²⁶

Summary.

The inversion rate of cane sugar in mixtures of light and heavy water at 25° C. was measured and was found to increase with the D₂O content, but not linearly. The increase in rate of this reaction and of the decomposition of diazo-acetic ester is attributed to an increase in concentration of the reacting complexes. A quantity proportional to the concentration of the complex can be computed according to a thermodynamic formula which is given and discussed. The decomposition of diazo-acetic ester is in complete agreement with the theory given. In the case of cane sugar inversion, there appear deviations which are small but obviously systematic, their possible causes are discussed. The relations between generalised acid catalysis and proton catalysis and the decrease and increase of the rate of protolytic reactions in heavy water, respectively, are discussed.

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We are also very much indebted to Miss K. Schiff, D.Phil., for her valuable assistance in discussing and preparing these papers.

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²¹ J. N. Brönsted, *Chem. Rev.*, 1928, **5**, 231.

²² E. A. Moelwyn-Hughes, R. Klar and K. F. Bonhoeffer, *Z. physik. Chem.* (A), 1934, **169**, 113; E. Pacsu, *J. Amer. Chem. Soc.*, 1933, **55**, 5056, and 1934, **56**, 745.

²³ J. N. Brönsted and I. E. Guggenheim, *J. Amer. Chem. Soc.*, 1927, **49**, 2554.

²⁴ A. Hantzsch and A. Weissberger, *Z. physik. Chem.*, 1927, **125**, 251.

²⁵ L. P. Hammet and M. A. Paul, *J. Amer. Chem. Soc.*, 1934, **56**, 830. On the other hand see C. M. Jones and W. C. McC. Lewis, *J. Chem. Soc.*, 1920, 117, 1120.

²⁶ E. A. Moelwyn-Hughes, *Z. physik. Chem.* (B), 1934, **26**, 281.

THE SURFACE COMPOSITION OF THE RUBBER GLOBULES IN HEVEA LATEX.

BY I. KEMP AND D. F. TWISS.

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The latex of *Hevea brasiliensis* consists of rubber globules suspended in a serum containing proteins, rubber "resin" (*i.e.* acetone-soluble substances) and methylinositol, together with smaller quantities of sugars and saline substances. The so-called "resin" of rubber has been shown by Whitby, Dolid and Yorston¹ to consist mainly of unsaturated fatty acids together with other fatty acids and sterols. As mentioned later the protein and fatty acids possibly may be partly in some form of association.

The colloidal properties of the latex will depend largely upon the amounts of the capillary-active substances (*i.e.* mainly proteins and "resin") adsorbed at the surface of the rubber globules. The influence of the protein on the behaviour of latex appears first to have been recognised by Weber.² Although Weber made his investigations with Castilleja latex and, contrary to present ideas, regarded the rubber in the latex globules as incompletely polymerised, his views on the existence of a surface film of protein steadily received wider acceptance, and it was early realised that they would apply also to the case of *Hevea* latex (which to-day is of paramount importance) although not to all natural latices generally.

This extension of the original observations was clearly stated by de Vries.³

The rubber "resin" on the other hand, judging by the experiments of Freundlich and Hauser,⁴ of Scholz,⁵ and of de Vries and Beumée-Nieuwland⁶ has little influence on the stability or behaviour of *Hevea* latex. Subsequently, however, Beumée-Nieuwland⁷ has postulated the presence of an adsorbed lipid layer in addition to the adsorbed protein. This theory has been further elaborated by Belgrave⁸ and van Rossem⁹ who assume the adsorption of a lipid-protein complex.

The recent rapid extension of latex-processes for rubber manufacture involving the need for initial stabilisation of *Hevea* latex and later adjustment of its stability to various degrees as necessary for different methods of use renders desirable as exact knowledge as possible of the character of the active protective substances in commercial latex.

¹ Whitby, Dolid and Yorston, *J.C.S.*, 1926, 1448.

² Weber, *Gummi Z.*, 1903, 17, 652; *Ber.*, 1903, 36, 3108.

³ De Vries, *Estate Rubber* (Druk Ruygrok and Co., Batavia), 1920, pp. 152-155; see also Belgrave, *Malayan Agric. J.*, 1923, 11, 348; van Rossem, *J. Soc. Chem. Ind.*, 1925, 44, 36T.

⁴ Freundlich and Hauser, *Koll. Z.*, 1925, 36, 19.

⁵ Scholz, *Kautschuk*, 1928, 4, 5.

⁶ De Vries and Beumée-Nieuwland, *Arch. Rubbercultuur*, 1927, 11, 498.

⁷ Beumée-Nieuwland, *ibid.*, 1929, 13, 555.

⁸ Belgrave, *Malayan Agric. J.*, 1925, 13, 369.

⁹ Van Rossem, *Colloid Chemistry*, by J. Alexander (Chemical Catalog. Co.), Vol. IV., 235 (1932).

The object of this paper is to describe the experimental determination of the fractions of the exposed surface of the rubber globule composed of protein and rubber "resin." The method employed is based upon the assumption that the resultant surface-charge density of a composite colloidal particle depends upon the surface-charge densities of the capillary-active substances adsorbed at the particle surface, and upon the fractions of the surface area occupied by those substances. In the case of the globules in Hevea latex, the rubber hydrocarbon surface is more or less occupied by a covering of protein or fatty-acid character. Thus if f_p , f_F be the fractions of the surface covered with protein and with "rubber-resin" respectively, f_R be the fraction of uncovered rubber surface, and σ_p , σ_F , σ_R be the surface-charge densities of the protein, "resin" and rubber surfaces respectively, then it is assumed that the resultant surface-charge density of the latex globule will be

$$\sigma = \sigma_p f_p + \sigma_F f_F + \sigma_R f_R \quad . \quad . \quad . \quad (1)$$

$$\text{or,} \quad \sigma - \sigma_R = (\sigma_p - \sigma_R) f_p + (\sigma_F - \sigma_R) f_F \quad . \quad . \quad . \quad (2)$$

It has previously been shown (Kemp¹⁰) that the relation between the cataphoretic mobility of a particle and its surface-charge density can be satisfactorily expressed by the equation of Henry,¹¹

$$u = \frac{\sigma}{\eta} \cdot \frac{\kappa a}{1 + \kappa a} f(\kappa a) \quad . \quad . \quad . \quad (3)$$

where u denotes the cataphoretic mobility, σ the surface-charge density, η the coefficient of viscosity of the solution, a the radius of the particle, κ is proportional to the square root of the ionic strength, and $f(\kappa a)$ is a function of κa . It follows from equation (3) that when the value of κa exceeds 100, the variation of mobility with particle-size is, for the present purposes, negligible, and in this case the mobilities of different particles are proportional to their surface-charge densities.

Thus equation (2) becomes

$$(u - u_R) = (u_p - u_R) f_p + (u_F - u_R) f_F \quad . \quad . \quad . \quad (4)$$

where u , u_p , u_F , u_R are the cataphoretic mobilities of particles of latex-rubber, of protein, of "resin" and of rubber hydrocarbon respectively.

The values of these different mobilities will depend upon the ionic environment of the particles. Thus, in one particular environment we have

$$(u' - u_R') = (u_p' - u_R') f_p + (u_F' - u_R') f_F \quad . \quad . \quad . \quad (5)$$

and in a second environment, providing f_p , f_F remain unchanged,

$$(u'' - u_R'') = (u_p'' - u_R'') f_p + (u_F'' - u_R'') f_F \quad . \quad . \quad . \quad (6)$$

Since the values of the mobilities in the two cases are readily determined by experiment, the value of f_p and f_F can be calculated.

In practice, the method was applied by determining the mobility— ρ_H relations in buffer solutions of ionic strength 0.01 for particles of pure rubber hydrocarbon, of protein, of "resin" and of latex-rubber. The value of κa was in no case less than 150, so that the effect of small variations in the particle size could be neglected.

¹⁰ Kemp, *Trans. Faraday Soc.*, 1935, **31**, 1347.

¹¹ Henry, *Proc. Roy. Soc.*, 1931, **A**, **133**, 106.

Experimental.

The measurements of electrophoretic mobility were made with a micro-cataphoresis apparatus of the capillary-tube type, in conjunction with a slit-ultramicroscope. Determinations of p_H were made by means of an antimony electrode.

The Rubber Hydrocarbon.

Crepe-rubber was extracted with acetone for 96 hours to eliminate the "resin." The rubber was then dissolved in chloroform and emulsified with alcohol and water containing caustic soda, the final concentration of alkali being approximately normal. The emulsion was repeatedly shaken with fresh quantities of caustic soda solution in order to free the rubber from proteins. The emulsion was finally washed until the p_H of the washings was less than 8. The emulsion was then stabilised with a little

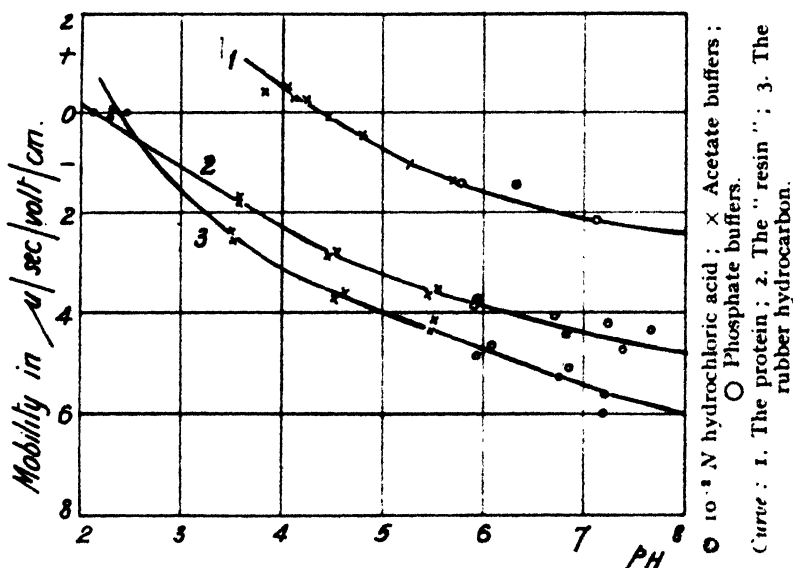


FIG. 1.—Constituent colloids of latex in solutions of ionic strength 0.01.

ammonia, the p_H being 9, and shaken vigorously with water. The aqueous dispersion of the purified rubber was then boiled under reduced pressure to remove the volatile solvents. The properties of the rubber dispersion were not affected by this boiling, since similar mobility values were obtained with dispersions from which the solvents had been removed by aeration.

The results for the dispersion of the rubber hydrocarbon are shown in Fig. 1, as curve 3. It will be seen that as the p_H is decreased, the negative charge on the rubber globules falls owing to the adsorption of hydrogen ions, and finally the charge becomes zero at $p_H 2.4 \pm 0.1$.

The Protein of Latex.

Ammonia-preserved plantation latex of 35 per cent. concentration was coagulated by dilute acetic acid, and the clear filtered "serum" was saturated with ammonium sulphate to precipitate the protein. The precipitate was filtered off, redissolved in acid of $p_H 2.0$, and reprecipitated with ammonium sulphate. The precipitate was collected, dissolved in water, and the excess electrolyte was removed by electrodialysis.

In order to determine the cataphoretic mobility of the protein, it was

necessary to make measurements with protein-covered silica particles, since the protein does not give sols containing visible particles. The results are given in Fig. 1 (curve 1). The isoelectric point of the protein or mixture of proteins in the solutions employed is $p_H 4.40 \pm 0.07$.

The "Rubber-Resin."

The acetone solution of "resin" obtained in the preparation of the rubber hydrocarbon was mixed with distilled water to give a dispersion of the "rubber-resin," excess acetone being removed by aeration. The mobility- p_H relation for "resin" particles is expressed as curve 2 of Fig. 1. The negative charge on the particles is due in part to the ionisation of the acids in the "resin," and partly to ionic adsorption. Thus, as the p_H is decreased, the ionisation of the acids is repressed, and in sufficiently acid solutions the adsorption of hydrogen ions is sufficient to reverse the charge, the isoelectric reaction being $p_H 2.1 \pm 0.1$.

The Latex.

Measurements were made with ammonia-preserved Hevea latex, of total solid content 39.1 grams/100 c.c., about five months after tapping.

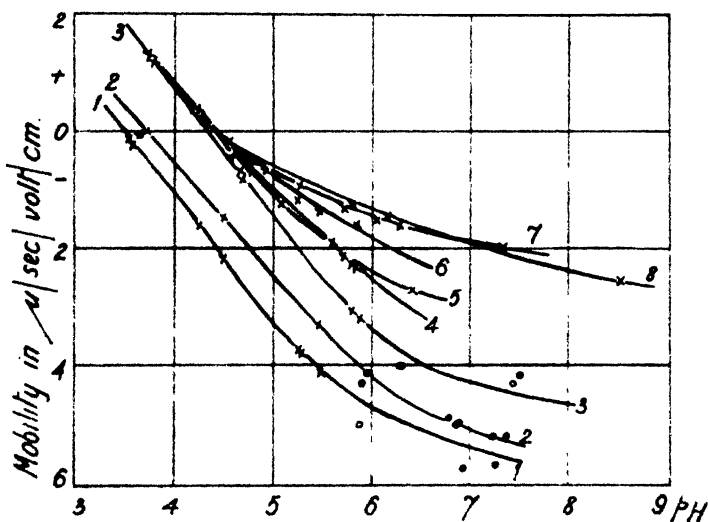


FIG. 2.—Diluted plantation latex in solutions of ionic strength 0.01.

× Acetate buffers; O Phosphate buffers.

Curve	1	2	3	4	5	6	7	8
Conc. of Latex per cent.	0.0016	0.008	0.39	1.18	3.91	6.76	8.98	19.5

Latices of various concentrations were prepared by diluting this plantation latex, and, in the case of the higher concentrations of latex, ionic impurities were removed by electrodialysis with a collodion membrane. The results are given in Fig. 2. From the graphs it will be seen that the cataphoretic behaviour of latex depends upon the degree of dilution.

Both the slope of the mobility- p_H curve and the isoelectric point of the latex dispersion are dependent upon the latex concentration. For low concentrations of latex, it was possible to make measurements over a large p_H range, but for higher concentrations, the measurement of mobility became difficult in solutions of $p_H > 7$, since usually in such solutions no aggregation of the latex globules took place, and owing to the large number of globules present, the intensity of reflected and diffracted light was too great for convenient observation.

Discussion.

The slopes of the mobility— p_H curves for latex of low concentrations are appreciably greater than those for the rubber hydrocarbon, the protein, and the "resin," indicating that the amounts of protein and of "resin" on the rubber surface may change continuously with p_H . Thus the solubilities of these two substances increase with p_H , and consequently in highly diluted latex, the rubber particles may be quite uncovered in alkaline solutions (Fig. 2, Curve 1).

In acid solutions (p_H about 4) the curves 3, 4, 5 of Fig. 2 indicate mobilities which are somewhat greater than those given by the protein curve (Fig. 1, curve 1). There is thus a slight discrepancy from the theory, since it would be expected that the slopes of the curves for latex would begin to fall on the acid side of the isoelectric points.

As the latex concentration is increased, the mobility— p_H curve approaches more nearly that of the protein, showing that the fraction of the globule surface covered with protein increases as the concentration of protein is increased. The curves for the highly diluted latex do not, therefore, obey the equation for the mobility— p_H slopes

$$\left(\frac{du}{dp_H} - \frac{du_R}{dp_H}\right) = \left(\frac{du_P}{dp_H} - \frac{du_R}{dp_H}\right)f_P + \left(\frac{du_F}{dp_H} - \frac{du_R}{dp_H}\right)f_F \quad (7)$$

hence the values of f_P and f_F cannot be derived from substitution in equations (5) and (6).

However, by a method of successive approximations, the values of f_P and f_F for the "average" latex globule at a given p_H can be calculated. At a particular p_H , the values of u , u_P , u_F , u_R can be measured, and, in addition, the approximate values of f_P and f_F can be obtained from the measured values of the mobilities, since near the isoelectric point, when the latex curve approaches the protein curve, we assume

$$f_P \doteq \frac{u - u_R}{u_P - u_R} \quad \text{and} \quad f_F = 1 \doteq f_P,$$

and by substituting these values in the equation (7), it is possible to obtain the theoretical value of du/dp_H at the p_H of measurement, since the slopes of the other curves are known at this p_H . From the approximate equation (7) and the more exact equation (4), the values of f_P and f_F can be obtained. The mobilities in equation (4) are correct to $\pm 5 - 7$ per cent., the slopes substituted in equation (7) are measurable to $\pm 10 - 15$ per cent., and the approximate values of f_P and f_F can be calculated to ± 10 per cent. near the isoelectric point. The errors in the final values of f_P and f_F vary with the p_H for the lower concentrations of latex, but do not exceed ± 10 per cent. at p_H 7. The errors are greater in the case of curves 1 and 2 of Fig. 2, where the protein covering appears to be incomplete at the isoelectric point.

By this method the change in the surface composition of the "average" rubber globule in latex with varying p_H could be obtained. The results are shown in Figs. 3 and 4.

In Fig. 5 is shown the variation in the surface composition of the "average" rubber-globule at p_H 8.0 as a function of the concentration of latex. It will be noted that the extreme surface of the "average" rubber globule is entirely composed of protein at this p_H when the concentration has risen to about 12 per cent. total-solids content.

Hence, the outer surface of the rubber globules in ordinary undiluted Hevea latex at p_H 8.0 is entirely of protein character, and the slope of the $f_p - p_H$ curve indicates that they are still completely covered at the

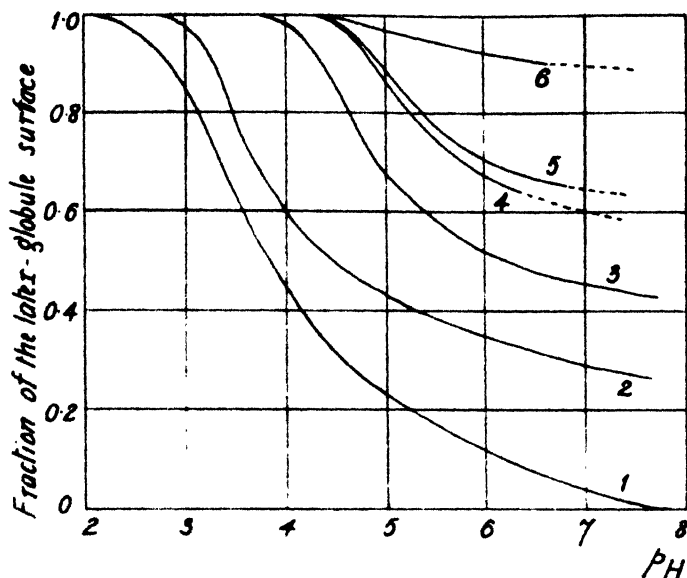


FIG. 3.—Relation between fraction of the globule-surface covered with protein and the p_H of the serum.

Curve	1	2	3	4	5	6
Latex Concn. per cent.	0.0010	0.098	0.39	1.18	3.91	6.76

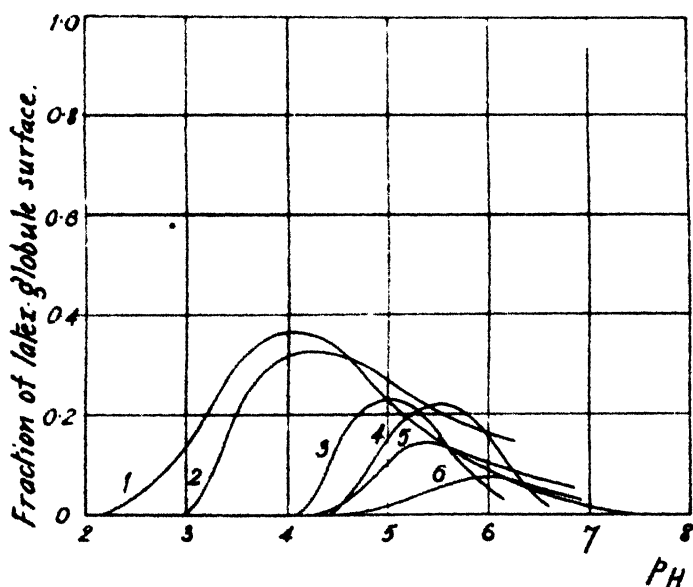


FIG. 4.—Relation between fraction of globule-surface covered with "rubber resin" and the p_H of the serum.

Curve	1	2	3	4	5	6
Latex Concn. per cent.	0.0010	0.098	0.39	1.18	3.91	6.76

p_H of the preserved latex, *i.e.*, p_H 10. Similarly, it is evident that the rubber globules in ammonia-preserved 60 per cent. latex (obtained by centrifugal creaming of ordinary plantation latex) are also completely covered with protein.

It should be noted that these results are not necessarily at variance with the possible presence of the protein as a lipoid-protein complex although they agree more naturally with the simpler view as to the independence of the protein and the "rubber-resin."

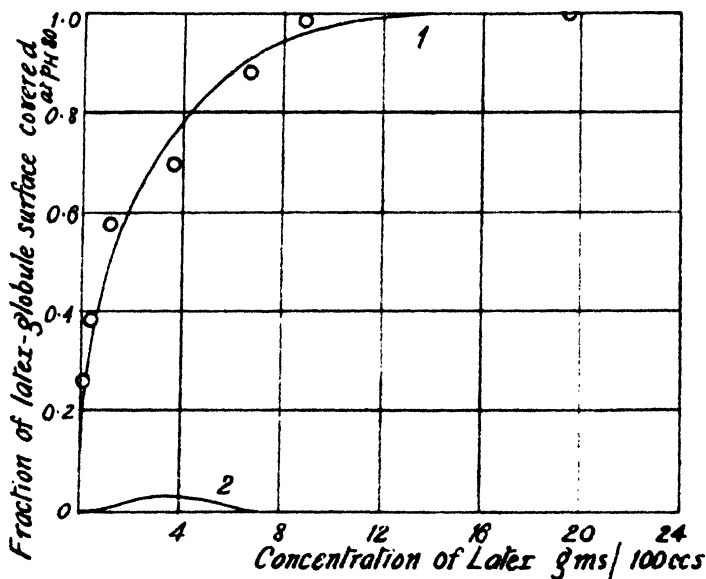


FIG. 5.—Variation in surface composition of rubber globule at p_H 8.0 with dilution of the latex. 1. Protein. 2. "Resin."

Summary.

1. A method for the surface analysis of colloidal particles is outlined.
2. The electrophoretic behaviour of the protein, "resin," and rubber hydrocarbon of the latex of *Hevea brasiliensis* is described.
3. The electrophoretic behaviour of the diluted ammonia-preserved plantation latex has been investigated, and it is shown that the amounts of protein and "rubber resin" adsorbed at the surface of the rubber globule are dependent upon the degree of dilution of the latex and upon the p_H of the serum.
4. The fractions of the rubber-globule surface covered with protein and with "rubber resin" are calculated, and their variation with latex-dilution and the p_H of the serum is plotted.
5. The rubber globules at p_H 8.0 are completely covered with a protein layer, provided the latex is not diluted below 12 per cent. total solids content.

The authors are indebted to the Dunlop Rubber Company Ltd., for permission to publish these results.

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THE TITRATION CURVE OF FEATHER KERATIN.

BY J. B. SPEAKMAN AND F. TOWNEND.

Received 23rd March, 1936.

Recent years have seen great advances in knowledge of the fine structure of animal fibres, but an exact knowledge of the composition of keratin, in terms of its constituent amino acids, seems to be needed if further progress is to be made. Although wool is the most important keratin from an industrial point of view, it would be difficult to accept it as the most suitable keratin for amino-acid analysis in view of its variable composition.¹ In addition, wool gives a very ill-defined X-ray fibre diagram and is not, therefore, a suitable subject for an attempt to obtain a complete interpretation of the structure of the keratin molecule from the combined results of X-ray and amino-acid analysis. On the other hand, feather keratin, particularly the quill of seagull feather, is remarkable for the perfection of its X-ray photograph, which is regarded as "the richest fibre photograph so far observed."² At the time seagull quill was selected for amino-acid analysis, however, its cell structure was believed to be homogeneous, but a recent examination of the cross-section of trypsin-retted quill has shown it to consist of at least two types of cell.

TABLE I.

Amino Acid.	Amount (g.) Isolated from 100 g. Feather.
Glycine	2.6
Alanine	1.8
Valine	0.5
Leucine	8.0
Proline	3.5
Serine	0.4
Aspartic acid	1.1
Glutamic acid	2.3
Tyrosine	3.6
Arginine	5.00
Lysine	1.04
Histidine	0.35

Although no work has been carried out on the composition of seagull quill, goose feather has been the subject of many investigations. Using the Fischer ester method, Abderhalden and Le Count³ obtained the data summarised in Table I, which also includes Block and Vickery's more recent determinations⁴ of the basic amino-acids in goose feather. Assuming that every amino-acid is incorporated in peptide chains through α -amino- and associated carboxyl-groups, the two sets of data account for only 35.4 per cent. of the feather. To this value must be added that for cystine, which according to Wilson and Lewis' results⁵ for different types of feather seems to be of the order of 9 per cent., as shown in Table II. In the case of goose feather, therefore, no more than 44 per cent. of the

¹ Speakman, *J. Soc. Dyers and Colourists*, 1934, *Jubilee Issue*, p. 36.

² Astbury, *Cold Spring Harbor Symposia on Quantitative Biology*, 1934, **2**, 21.

³ Abderhalden and Le Count, *Z. physiol. Chem.*, 1907, **83**, 348.

⁴ Block and Vickery, *J. Biol. Chem.*, 1931, **93**, 113.

⁵ Wilson and Lewis, *ibid.*, 1927, **73**, 543.

keratin has been identified, but the preceding data, even though incomplete, have a definite value in connection with later argument concerning the composition of feather keratin.

As a preliminary to analytical work on seagull quill, it was decided to determine its titration curve, because corresponding work on wool keratin ⁶ together with related studies of its elastic properties in media ⁷ of varying p_H , have proved useful in giving a general indication of the constitution of the molecule. For example, if seagull quill is similar to wool, its maximum acid-combining capacity should establish the content of basic amino-acids and show whether Block and Vickery's determinations of the basic amino-acids in goose feather are valid for seagull quill. Alternatively, if there is any foundation for Astbury's enquiry as to whether it may not be that "the growth of feathers finds its origin in the

TABLE II.

Kind of Feather.					Cystine (per cent.).	Sulphur (per cent.).	Nitrogen (per cent.).
Turkey (1)	Fan				7.1	2.44	15.1
	Quill				8.9	2.40	15.8
Turkey (2)	Fan				7.7	—	14.8
	Quill				7.7	—	15.5
Goose	Fan				10.7	3.00	15.1
	Quill				9.1	2.53	—
Duck	Fan				12.2	2.00	15.5
	Quill				8.8	—	15.9

development of further keratin chains by the formation of *lateral* peptide linkages? " ⁸ the maximum acid-combining capacity of feather should be less than would be expected from the content of basic amino-acids. Finally, the titration curve of wool keratin shows an isoelectric range from p_H 5 to 7, which implies equivalence between the dicarboxylic acids and the amide nitrogen and basic amino-acids. Should the titration curve of feather keratin show a similar isoelectric range, the same equivalence rule would hold, and the total content of dicarboxylic acids in seagull quill would then be capable of deduction.

Experimental.

Purification of Feather.—Because there is little difference between the X-ray photographs of feather from various types of gull, and because of the difficulty of collecting large quantities of material for analysis, the tail and wing feathers of mature herring gull, black-backed gull and gannet were purified and mixed as follows. After rejecting those quills which showed an opaque white spotting, the remainder were cut just below the first barbs, at the junction of the translucent quill and the pith-containing portion of the rachis. The inferior umbilicus of each quill was then cut away, the feather sheath removed from the outside, and the quill bisected longitudinally. After cleaning each half by scraping both sides with a knife, the quill was cut into pieces from $\frac{1}{4}$ to $\frac{1}{2}$ inch long. When a sufficient quantity of quill had been prepared in this way, it was freed from wax by extraction in an all-glass soxhlet apparatus for two days with alcohol, two

⁶ Speakman and Stott, *Trans. Faraday Soc.*, 1934, **30**, 539.

⁷ Speakman and Hirst, *ibid.*, 1933, **29**, 148.

⁸ Astbury and Marwick, *Nature*, 1932, **130**, 309.

days with ether, and two days again with alcohol. Finally, the alcohol retained by the feather was removed by washing in several changes of distilled water over a period of 3 or 4 days.

Determination of the

Titration Curve.—Since the isoelectric point or region of feather keratin was unknown, the purified feather was merely allowed to attain equilibrium with distilled water at 22.2° C., the final p_H being 4.6, before being used for determinations of acid- and alkali-combining capacity. Approximately 1-gram samples of the air-dry keratin were dried over phosphorus pentoxide *in vacuo* until constant weight was attained, a period of two months or more being necessary. Except at low p_H , where 2 g. of feather were used to increase the precision of the results, each 1-gram sample was transferred to 100 cc of HCl or NaOH solution of known p_H at 22.2° C., precautions being taken

to exclude carbon dioxide from the alkaline solutions during equilibration and p_H measurement. Preliminary experiments showed that equilibrium was attained between feather and acid and alkaline solutions in 5 and 10 days respectively, such long times being necessary because the feather was used in fairly large pieces. The amounts of acid and alkali combined with the feather were calculated from the measurements of initial and final p_H , except at extremes of p_H , where aliquots of the original and equilibrium solutions were titrated with alkali or acid. From the results, which are collected in Table III, the titration curve shown in Fig. 1 was constructed.

TABLE III.

Reagent.	Final p_H .	C.c. $N/12$ Acid or Alkali Combined with 100 g. dry Feather.	
		p_H .	Titration.
Hydrochloric acid	0.20	—	39.1
	0.58	—	40.9
	0.97	—	40.4
	1.35	—	36.9
	1.76	—	30.7
	2.17	—	24.0
	2.48	17.8	19.2
	2.98	8.0	—
	3.33	5.3	—
	4.20	0.3	—
Sodium hydroxide	4.76	0.0	—
	5.17	0.0	—
	5.42	0.4	—
	6.57	0.5	—
	7.22	0.6	—
	7.31	2.5	—
	7.46	1.1	—
	7.95	3.0	—
	8.75	5.4	—
	9.93	11.1	—
	10.21	14.0	—
	10.90	22.4	—
	11.54	—	37.0

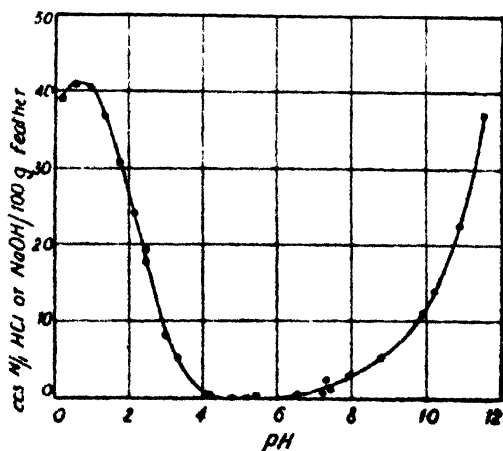


FIG. 1.

Discussion of Results.

If the basic amino-acids of feather are incorporated in long peptide chains through α -amino and associated carboxyl groups, as in the case of wool, acid must combine with feather through the terminal amino-, guanido- and iminazole-groups of lysine, arginine and histidine, respectively. Taking Block and Vickery's data for the amounts of these amino-acids in goose feather, its maximum acid-combining capacity should be 38.1 c.c. of $N/1$ hydrochloric acid per 100 g. dry feather, a value in good agreement with that found experimentally for seagull quill, *viz.*, 41 c.c. That the theoretical result should be low is understandable in view of the great difficulty of isolating basic amino-acids quantitatively, and it seems reasonable to assume that Block and Vickery's determinations of the basic amino-acids in goose feather are equally valid for seagull quill. Support for this view is to be found in the following approximate determination of the arginine content of seagull quill by the van Slyke procedure.

49.49 g. dry seagull quill were hydrolysed by boiling for 30 hours with 400 c.c. of 20 per cent. hydrochloric acid under a reflux condenser. After concentration to a syrup, the solution was made alkaline with lime, diluted to 2 litres, and distilled under reduced pressure. From the amount of ammonia evolved, the amide nitrogen content of the feather was found to be 15.12 mgm./g., but the best value, as deduced from 10 determinations on three hydrolysates, is 14.90 mgm./g. Following the determination of amide nitrogen, the lime was filtered off and washed well with hot water. The filtrate was then made up to two litres after neutralisation with hydrochloric acid, and 350 c.c. of concentrated hydrochloric acid were added. After heating the solution to 90° C. on the water bath, the bases were precipitated by adding 250 g. phosphotungstic acid dissolved in 1 litre of water. The phosphotungstates were allowed to separate for three days in the ice chest, before being filtered off and washed in four litres of an ice-cold solution of 2.5 per cent. phosphotungstic acid in $N/1$ hydrochloric acid. Amyl alcohol-ether mixture, previously extracted with hydrochloric acid, was used to redissolve the base-phosphotungstates in the manner recommended by van Slyke, and the solution was made up to 500 c.c. The total nitrogen content of the phosphotungstates was found to be 1654.0 mgm., or 33.41 mgm./g. dry seagull quill. This value is far in excess of what would be expected from Block and Vickery's determinations of the basic amino acids in goose feather, but it is well known that the precipitate of phosphotungstates is liable to contain amino-acids other than the hexone bases.* When the phosphotungstates were allowed to separate at room temperature instead of at 0° C., the nitrogen content of the precipitate was equivalent to 24.82 mgm./g. From this value must be subtracted 5.00 mgm./g. for the cystine content of the precipitate, as shown below, so that the nitrogen content of the basic amino-acids in seagull quill is 19.82 mgm./g. While this result accords well with the theoretical value of 19.1 mgm./g. deduced from Block and Vickery's determinations of the basic amino-acids in goose feather, too much stress cannot be placed on the agreement because the quantity of amino-acids precipitated by phosphotungstic acid varies with temperature.

As regards the main solution of the phosphotungstates precipitated at 0° C., aliquots were boiled with 50 per cent. caustic potash solution for six hours, and six determinations of the amount of ammonia evolved gave an average value of 10.83 mgm. nitrogen per 10 c.c. of solution. The latter contained cystine, which, according to van Slyke, liberates 18 per cent. of its nitrogen as ammonia under the above conditions. Two determinations by the Benedict-Denis method of the amount of sulphur in the solution of phosphotungstates showed that the cystine nitrogen was 4.99 mgm./10 c.c., so

*Kernot and Knaggs, *Biochem. J.*, 1928, **22**, 528; Kernot, Knaggs and Speer, *ibid.*, 1930, **24**, 379.

that the correction to be applied to the above value for the nitrogen liberated on boiling the phosphotungstates with caustic potash is 0.90 mgm. Since arginine liberates half its nitrogen as ammonia under the above conditions, the total arginine nitrogen is $2 + 9.93$ mgm. per 10 c.c. of the solution of phosphotungstates, or 20.07 mgm./g. of feather, and the arginine content of the feather is 6.23 per cent. That this value should exceed that obtained by Block and Vickery is not surprising in view of the fact that the isolation method yields low results, and the van Slyke method high results. Actually, some increase in the arginine content of feather above Block and Vickery's value is needed to account completely for its acid-combining capacity, so that the above determination of the arginine content of seagull quill serves to confirm the view that Block and Vickery's data for goose feather are equally applicable to seagull quill. It must therefore be concluded that the maximum acid-combining capacity of feather keratin is accounted for by the basic side chains of arginine, lysine and histidine, and the balance of evidence is opposed to the possibility* that the terminal amino- and guanido-groups of lysine and arginine may take part in the formation of lateral peptide linkages.

The second point of interest in the titration curve of seagull quill is the fact that it shows an isoelectric range from about p_H 4.3 to 6.3. By analogy with wool, which shows a similar range from p_H 5 to 7, the isoelectric range of feather may be taken to imply equivalence between its dicarboxylic acids and the basic amino-acids and amide nitrogen. According to this view, the dicarboxylic acid nitrogen of feather should be 14.90 (amide nitrogen) + 5.34 (basic amino-acids) = 20.24 mgm./g. As shown in Table I., however, the amounts of dicarboxylic acid isolated from goose feather fall far short of this requirement, and correspond with only 3.38 mgm. nitrogen per gram of feather. The discrepancy is so great that the total quantity of dicarboxylic acids in seagull quill was estimated in the following manner. In the preceding determination of arginine, the solution remaining from the precipitation of phosphotungstates contained the dicarboxylic acids of 49.49 g. of feather keratin. It was freed from phosphotungstic acid by extraction with amyl alcohol-ether mixture and then concentrated under reduced pressure to remove excess hydrochloric acid. After making the syrup strongly alkaline with lime, it was diluted to a volume of 1 litre, and the calcium salts of the dicarboxylic acids in 600 c.c. of the solution were precipitated with eight volumes of alcohol. When the mixture had stood overnight, the precipitate was filtered off and washed well with alcohol. Damodaran's procedure¹⁰ for estimating dicarboxylic acids was not followed, because it was found that the presence of calcium chloride in the solution of the calcium salts of dicarboxylic acids interfered greatly with their precipitation by alcohol, the precipitate being far too impure to afford a reliable estimate of the dicarboxylic acid content of seagull quill. The impure calcium salt precipitate was therefore redissolved in warm water, filtered to remove a slight turbidity, and then made up to a volume of 2 litres. Aliquots of the solution were withdrawn and precipitated with various volumes of alcohol, the nitrogen content of the precipitates being determined by Kjeldahl's method. The results are summarised in Table IV., illustrated by Fig. 2.

The curve shows an abrupt break when the nitrogen content of the precipitate is 20 mgm./g. feather, a value in remarkably close agreement with the theoretical requirement of 20.24 mgm./g. for the nitrogen content of the dicarboxylic acids in seagull quill. It is therefore evident that the dicarboxylic and basic amino-acids are incorporated in peptide chains through α -amino- and associated carboxyl-groups. A large part of the acid side chains are combined with ammonia to form acid amides, the remainder being combined with the basic side chains to form salt linkages of the type previously shown to exist in wool keratin.⁷ Just as in the latter case, there

¹⁰ Damodaran, *Biochem. J.*, 1931, **25**, 2123.

is exact equivalence between the basic side chains and those acid side chains not present as acid amides. With both wool and feather keratin, the presence of the necessary amount of dicarboxylic acids to account for amide nitrogen and basic amino-acids according to the salt linkage hypothesis, has also been demonstrated in large-scale attempts to isolate the acids. As regards feather keratin, separation of the acids from the mixture is not yet complete,

TABLE IV.

Volumes of Alcohol Added.	Nitrogen in Precipitate (mgm./g. Feather).
1	3.16
2	12.32
3	18.25
4	19.87
6	20.53
9	21.21
12	22.55

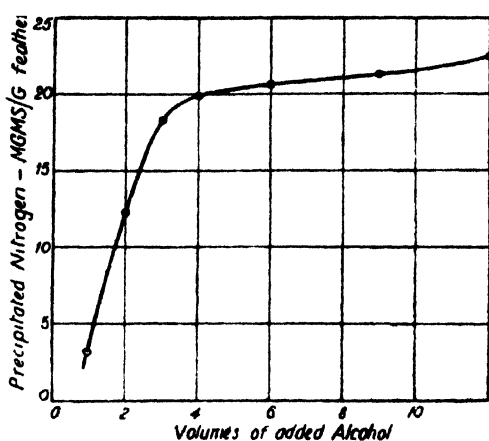


FIG. 2.

but 9.1 per cent. of glutamic acid and 2.4 per cent. of *i*-aspartic acid have so far been isolated, corresponding with a dicarboxylic acid nitrogen content of 11.3 mgm./g. of feather.

In conclusion, it will be observed that the titration curve of feather keratin, unlike that of wool, does not show the step due to lysine salt linkages at p_H 10 to 11. No significance need be attached to its absence because the quill undergoes destructive attack in the more strongly alkaline solutions during the 10 days needed to attain equilibrium.

Summary.

The titration curve of seagull quill shows an isoelectric range from p_H 4.3 to 6.3, suggesting that the dicarboxylic acids are exactly equivalent to the basic amino-acids and amide nitrogen. Support for this, the salt-linkage hypothesis, has been derived from determinations of the amide nitrogen and dicarboxylic acid contents of the keratin. The dicarboxylic acids were found to be equivalent to the amide nitrogen and the basic amino-acids, the latter being estimated from the maximum acid-combining capacity, which accords well with Block and Vickery's determinations of the basic amino-acids in goose feather.

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THE DECOMPOSITION OF HYDROGEN SULPHIDE AND WATER ON MOLYBDENUM FILAMENTS.

By F. E. T. KINGMAN.

Received 24th March, 1936.

In the course of an investigation of molybdenum catalysts some preliminary studies have been made of the decomposition of hydrogen sulphide and water on molybdenum filaments.

Apparatus.

The molybdenum filament, 20 cm. long and 0.006 cm. diameter was spotwelded at each end to stout tungsten leads fused through the ends of the pyrex reaction vessel, which was cylindrical in form, 25 cm. long, and 2.5 cm. diameter. The reaction vessel was connected to a Pirani gauge and gas pipette, and the whole apparatus could be evacuated to 10^{-5} mm. by a mercury pump backed by a Cenco "Hyvac" oil pump.

The Pirani gauge consisted of a platinum filament maintained at 100° C. Blank experiments showed that no decomposition of either hydrogen sulphide or water took place on this filament. The gauge was calibrated for hydrogen against a McLeod gauge, which was cut off from the reaction system during experiments.

The temperature of the molybdenum filament was determined by measuring its resistance and calculating from the resistance-temperature curve for molybdenum; no corrections were made for variation in temperature along the filament.

1. Experiments with Hydrogen Sulphide.

Hydrogen sulphide prepared from hydrochloric acid and antimony sulphide, was washed with water, dried over phosphorus pentoxide, and distilled. Hydrogen was purified by passage through a heated palladium tube.

Experiments were carried out by admitting 0.03 c.c. of hydrogen sulphide, giving an initial pressure of 0.088 mm., and following the course of the reaction by freezing out the residual hydrogen sulphide with liquid air and measuring the pressure of hydrogen on the Pirani gauge.

Results.—The results obtained from experiments at temperatures of 400°–685° C. are shown in Fig. 1, the logarithm of the residual pressure of hydrogen sulphide being plotted against the time. Analysis of the results showed that the reaction could be accurately represented by a mono-molecular equation, *i.e.*,

[illegible]

whence $k = \frac{I}{t} \log_e \frac{p_0}{p}$ (2)

where

p = pressure of hydrogen sulphide at time t .
 p_0 = initial pressure of hydrogen sulphide,

p_0 = initial pressure of hydrogen sulphide,

so that, since the decomposition of hydrogen sulphide results in the liberation of an equal volume of hydrogen,

$$p_0 - p = \text{pressure of hydrogen at time } t.$$

For a constant value of p_0 ,

$$kt = A - \log_e p \quad (A = \log p_0)$$

or

$$k_1 t = B - \log_{10} p.$$

Thus by plotting the values of $\log_{10} p$ against t for various temperatures, a series of straight lines are obtained (Fig. 1) from the slopes of which the relative value of k can be determined for each temperature. From the values thus obtained, the energy of activation can be calculated using the usual Arrhenius equation. The heat of activation for this reaction was thus found to be 25,000 Cals.

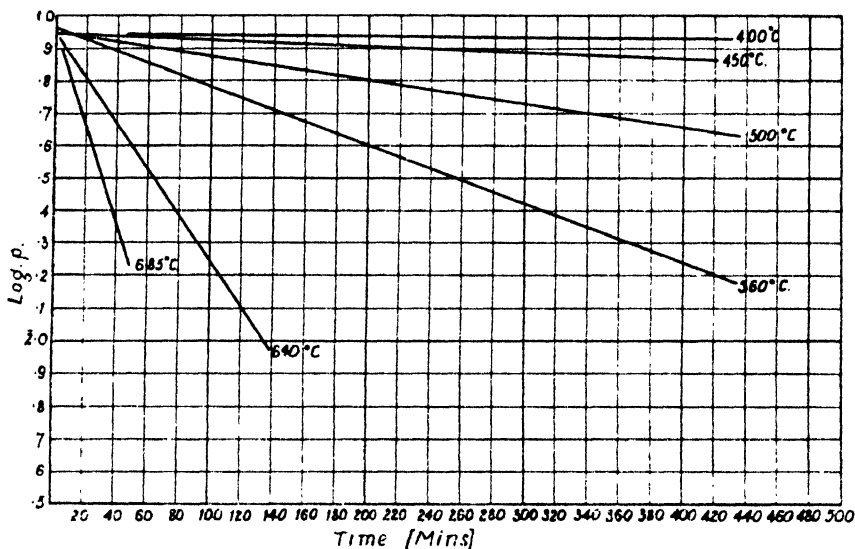


FIG. 1.

The decomposition of hydrogen sulphide must result in the liberation of an equimolecular amount of hydrogen, and, in addition, the production of free sulphur or of molybdenum sulphide. In these experiments it was observed that after 0.9 c.c. of hydrogen sulphide had been decomposed, the solid product of the reaction became visible as a dark continuous film on the walls of the reaction vessel. This product was distilled into a small liquid-air trap, the latter cut off, and the product examined. Owing to the small amount available, it was not possible to analyse the product completely, but it was shown that no molybdenum was present. This result was checked by comparing the weight of the filament with that of an equal length of the original molybdenum wire; there was no change in weight.

Thus, the decomposition of hydrogen sulphide on a molybdenum filament under the conditions of these experiments results in the formation of hydrogen and free sulphur. No production of molybdenum sulphide takes place, the sulphur formed being continuously removed by evaporation from the filament and condensation on the cold walls of the reaction vessel. This is also in agreement with the experimental fact that no inhibition of the reaction by the products can be observed.

2. Decomposition of Water Vapour.

The apparatus used was similar to that described above. A tube containing water (freed from dissolved gases) was kept in melting ice, thus maintaining a constant vapour pressure, and a known volume of water vapour at this pressure was admitted to the reaction system so as to give an initial pressure of water vapour of 0.1 mm. The course of the reaction was followed by a similar method to that employed in the hydrogen sulphide experiments, the water vapour being frozen out at intervals by liquid air, and the residual pressure of hydrogen measured on the Pirani gauge.

It was found that no appreciable reaction could be observed at temperatures below 800° C., the experiments described were therefore carried out at 800°-1200° C., and some typical results are shown in Fig. 2.

The reaction which occurred resulted in the formation of a film of molybdenum oxide on the surface of the filament. At temperatures below 1000° C. this film was not volatilised and retarded the reaction. Thus, when a second admission of water vapour was made at 800° C., the rate

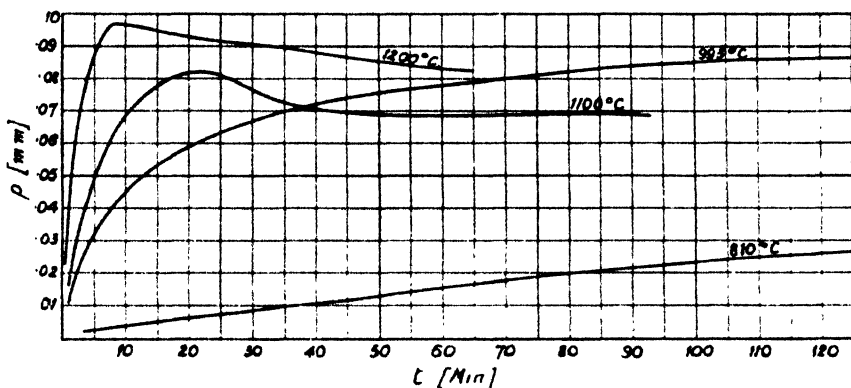


FIG. 2.

of reaction fell to a negligible value. The oxide film could easily be removed by flashing for a short time at 1500° C.

At temperatures above 1000° C. it was found that the oxide film volatilised as quickly as it was formed, so that when a second admission of water vapour was made without flashing the wire, the rate of reaction was the same as with a flashed filament.

In these experiments carried out at temperatures above 1000° C., it was also observed that the pressure of hydrogen, after increasing steadily to 0.07-0.08 mm. became constant and then slowly decreased. This phenomenon was not quantitatively reproducible, the magnitude of the decrease in pressure being dependent on factors apparently outside the degree of experimental control. This decrease in pressure can be accounted for by assuming that some of the hydrogen molecules are dissociated at the heated filament and the atoms are then taken up by the molybdenum oxide film on the walls of the reaction vessel, the capricious nature of the effect being due to variations in the surface of this film.

The pressure-time curves for the decomposition of water vapour are thus more complex than those obtained in the hydrogen sulphide experiments, and it has not been possible to analyse the results even for the early stages of the reaction, where the secondary reaction involving the disappearance of hydrogen might be expected to have less effect. The heat of activation of the primary process of the decomposition of water to give hydrogen and molybdenum oxide has been obtained by determining the

time (t) taken to produce a definite pressure of hydrogen. The heat of activation is then calculated from the formula :

$$2.303 \log_{10} \frac{t_1}{t_2} = \frac{Q}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

where t_1 and t_2 are the times taken to reach a given pressure at temperatures T_1 and T_2 respectively.

Plotting $\log t$ for the times taken to give pressures of 0.01, 0.02 and 0.03 mm. against $1/T$ for temperatures of 800°-1200° C., a series of three straight parallel lines are obtained (Fig. 3) from which the value of the energy of activation is 43,000 Cals. It will be noted that at low concentrations of the oxide film there is no change in the activation energy of the reaction as the temperature is increased beyond that necessary to volatilise the oxide film.

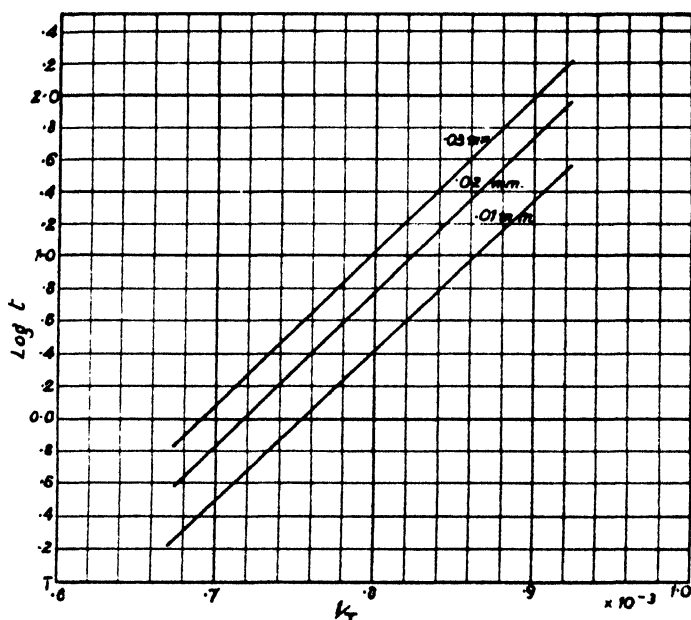


FIG. 3.

Summary.

1. The decomposition of hydrogen sulphide at a pressure of 0.1 mm. on a molybdenum filament has been studied over a temperature range of 400°-685° C. The reaction results in the formation of hydrogen and free sulphur, the rate of reaction being proportional to the pressure of hydrogen sulphide. The energy of activation of the reaction is 25,000 Cals.

2. The decomposition of water vapour on a similar molybdenum filament at temperatures of 800°-1200° C. results in the formation of molybdenum oxide and hydrogen, followed, at temperatures above 1000° C. by the formation of hydrogen atoms, which are absorbed by the molybdenum oxide film on the walls of the reaction vessel. The heat of activation of the decomposition reaction is 43,000 Cals.

The writer, who is a member of the research staff of the Department of Scientific and Industrial Research has carried out this work in the

Department of Colloid Science, Cambridge, under the direction of Professor Rideal.

The author's thanks are due to Professor Rideal and to Dr. J. K. Roberts for their interest and advice.

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KINETICS OF RECOMBINATION OF BROMINE-ATOMS II.

BY E. RABINOWITCH AND W. C. WOOD.

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I. Introduction.

In a previous paper¹ we described an optical method for the determination of the stationary dissociation of Br_2 molecules in an illuminated vapour. Because of thermal effects we were unable to calculate the exact degree of dissociation except when the dissociation takes place in a helium atmosphere. Later² we found that thermal effects can be reduced by using smaller halogen-concentrations. This is shown by comparing the formulæ (1) and (2), derived¹ for the two effects in question :

$$\Delta_{\text{therm.}} = \frac{3}{32} \frac{Q}{\kappa T_0} (\simeq \text{const.} \times [\text{Br}_2]) \quad (1)$$

$$\Delta_{\text{homo. diss.}} = \frac{1}{[\text{Br}_2]} \sqrt{\frac{2N_{\text{hv}}}{C_1[X]}} \left(\simeq \text{const.} \times \frac{1}{\sqrt{[\text{Br}_2]}} \text{ if } [X] = \text{const.} \right) \quad (2)$$

$$\frac{\Delta_{\text{therm.}}}{\Delta_{\text{homo. diss.}}} = \text{const.} \times [\text{Br}_2]^{\frac{3}{2}} \quad (3)$$

$\Delta \left(= \frac{\Delta[\text{Br}_2]}{[\text{Br}_2]} \right)$ is the relative change of concentration of bromine-molecules caused by illumination, Q the energy (in Cals.) and N_{hv} the number of quanta absorbed per sec. per c.c. of the gas, $[X]$ the concentration of molecules acting as third bodies in the recombination of the atoms, κ the thermal conductivity, and C_1 the velocity constant of the recombination. At low concentrations of bromine, Q and N_{hv} are proportional to $[\text{Br}_2]$.

The darkened areas in Figs. 3a and 3b show the parts played by the thermal effects : (A) in the old experiments with 4.5 mm. of Br_2 , and (B) in the new experiments with a Br_2 pressure about 0.3 mm.

II. Experimental.

The scheme of the apparatus was shown in Fig. 1 in the previous papers.^{1, 2} The second paper² contains also the description of the exact computation of N_{hv} . Fig. 1 shows the spectral energy-distribution of the

¹ E. Rabinowitch, H. L. Lehmann, *Trans. Faraday Soc.*, 1935, **31**, 689.

² E. Rabinowitch, W. C. Wood, *J. Chem. Physics*, 1936.

light L from the 1500 watt carbon arc used for dissociation, filtered through 1 cm. of saturated CuSO_4 -solution. The lower curve shows the intensity

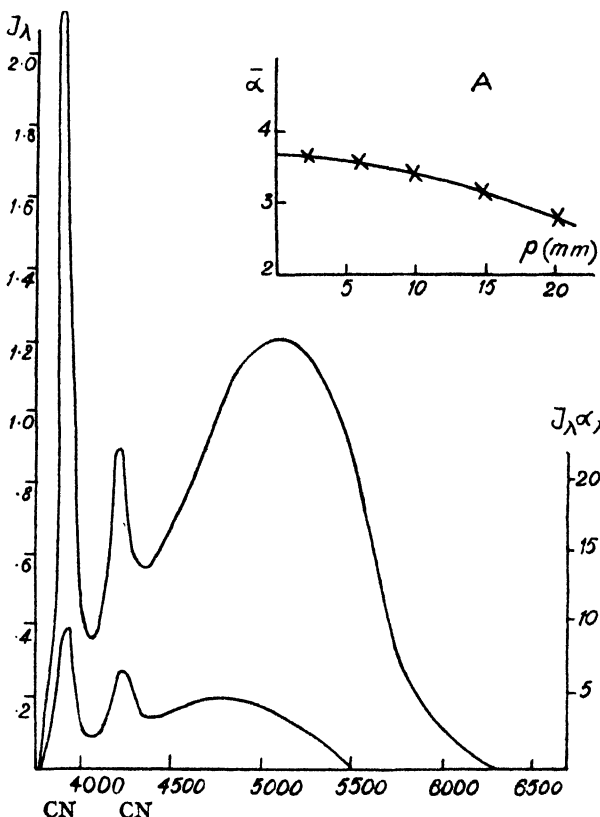


FIG. 1.—Energy-distribution of the illuminating light L , and its absorption by bromine.

distribution of the light absorbed by bromine.³ By graphical integration, the mean extinction coefficient of bromine for the light L , and the mean wave-length of the light absorbed were found to be,

$$\bar{\alpha}_L = 3.75 \\ \lambda_L = 4330 \text{ \AA.}$$

The first value was confirmed by direct measurement of the absorption of L -light by bromine at higher pressures and extrapolation to $p(\text{Br}_2) = 0$ (Fig. 1 A inset). The mean absorption of L -light in the cell was less than 2 per cent. With the above-calculated values of $\bar{\alpha}_L$ and λ_L , and the calibration-factor of the thermopile-galvanometer combination deter-

mined previously, the following formulæ were derived for the calculation of N_{hv} and Q :

$$N_{hv} = 1.99 \times 10^{13} \times p_{\text{mm.}}(\text{Br}_2) \times L_{\text{cm.}} \frac{\text{quanta}}{\text{sec.} \times \text{c.c.}} \quad (4)$$

$$Q = 2.21 \times 10^{-6} \times p_{\text{mm.}}(\text{Br}_2) \times L_{\text{cm.}} \frac{\text{g cal.}}{\text{sec.} \times \text{c.c.}} \quad (5)$$

L being the deflection of the galvanometer in cm.

The light beam J from a 6v. filament lamp, used for the measurement of $[\text{Br}_2]$ and $\Delta[\text{Br}_2]$, was filtered through infra-red-absorbing glass (Jena BG17) and blue glass (Jena BG12). It contained wave-lengths 4000–4800 Å. and the mean extinction-coefficient of bromine for it was found to be (at low pressures) $\bar{\alpha}_J = 6.0$. The absorption of J along the cell ($d = 12$ cm.) is 7–10 per cent. only, and the use of a mean $\bar{\alpha}$ -value is therefore justified.

³ Cyanogen-bands are prominent in the part of the spectrum strongly absorbed by bromine; this affects somewhat the exactness of the determination of N_{hv} , because the intensity of these bands is variable even when the arc burns very steadily. The extinction coefficients used for calculation were those given by Ribaud; we tested several points of his curve and found them to be correct.

The relative change of concentration $\Delta \equiv \frac{\Delta[\text{Br}_2]}{[\text{Br}_2]}$ was calculated from the relative change of transmission $\Delta J/J$ by means of the equation⁴

$$\Delta J/J = \Delta \times \bar{\alpha}_J p_{\text{atm.}}(\text{Br}_2) \left. \frac{d \log_e 10}{p_{\text{mm.}}(\text{Br}_2)} \right\} \times \Delta \quad (6)$$

By using (4) and (6) for the determination of N_{av} and Δ respectively, the velocity-constant C_1 in (2) was calculated from measurements of ΔJ , J and L .

The bromine-pressure was measured by means of a manometer filled with sulphuric acid. Another method—which gives more exact values at low pressures—is to calculate $p(\text{Br}_2)$ from the absorption of the light J , using the above-determined extinction-coefficient $\bar{\alpha}_J = 6.0$.

III. General Results.

We determined the stationary dissociation of illuminated Br_2 in mixtures with He , H_2 , N_2 , O_2 , CH_4 and CO_2 . Figs. 2 and 3 show, as

examples, the results obtained with H_2 and N_2 . The abscissæ are the pressures of the gases in mm., the ordinates the observed changes in transmission ΔJ . The thermal effect (shown by the darkened area) forms the whole of the effect observed in pure bromine, but only a small part of it in presence of foreign gases. The unbroken lines in Figs. 2 and 3 are the "theoretical" curves: straight lines in the region of heterogeneous recombination, (where the molecules recombine on the walls) and inverse-square-root curves in the region of homogeneous recombination (according to equation (2)). The agreement between experiment and theory is remarkable.⁵

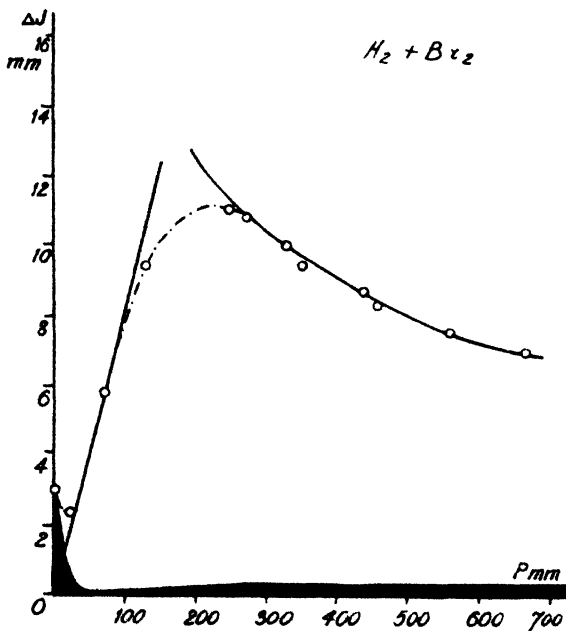


FIG. 2.—Effects observed in hydrogen.

The dependence of the effect on light intensity L is shown by Fig. 4. The abscissæ are the pressures $p_{\text{mm.}}$ (X) (X = argon in this particular case) and the ordinates the exponents α of the equation

$$\Delta J = \text{const.} \times L^\alpha \quad (7)$$

⁴ The method, by which Δ can be calculated at higher $p(\text{Br}_2)$ values is described in the last part of this paper.

⁵ We discussed elsewhere—see *Z. physik. Chemie (B)*, 1936, why the influence of the homogeneous recombination is relatively strong at low pressures, whereas that of the wall recombination disappears as soon as the maximum of ΔJ is passed.

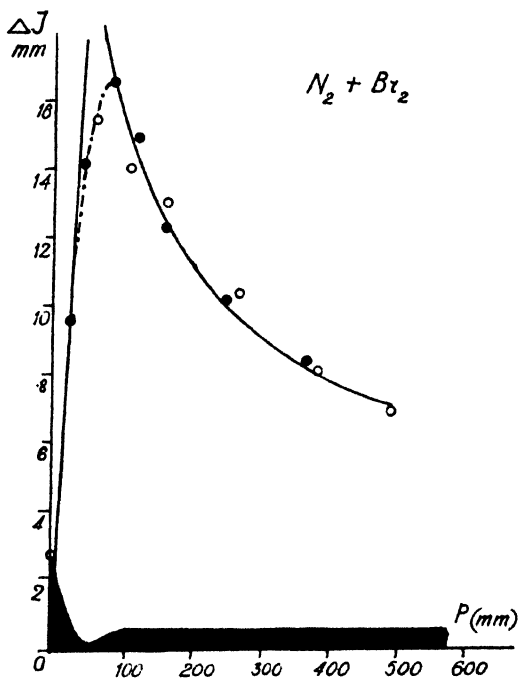


FIG. 3a.—Effects observed in nitrogen;
 $p_{(\text{Br}_2)} = 0.28 \text{ mm.}$

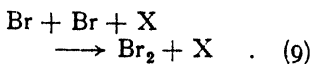
The value of x drops from $x = 1$ (which is the theoretical value for both the thermal effect and the *heterogeneous* dissociation equilibrium) to $x = \frac{1}{2}$, which is the value required by (2) for the homogeneous dissociation-effect.

In the case of bromine a large range of halogen pressures can be used. The relative change of transmission $\Delta J/J$ must be proportional to $p^2_{(\text{Br}_2)}$ in the case of the thermal effect, to $p_{(\text{Br}_2)}$ in that of the heterogeneous dissociation-effect and to $\sqrt{p_{(\text{Br}_2)}}$ in the case of the homogeneous dissociation. Fig. 5 shows the value of the exponent γ in the equation:

$$\Delta J/J = \text{const.} \times [\text{Br}_2]^\gamma \quad (8)$$

as a function of $p_{(\text{Br}_2)}$, (for the case of helium as third body). The results are in full agreement with theory.

The validity of formula (2) for the region of homogeneous recombination is thus proved in respect of the dependence of the effect on bromine pressure, light intensity and pressure of the foreign gas. This shows, that the recombination process is described by the simple equation



Formation of Br_3 or of other complexes does not intervene markedly in the recombination process.

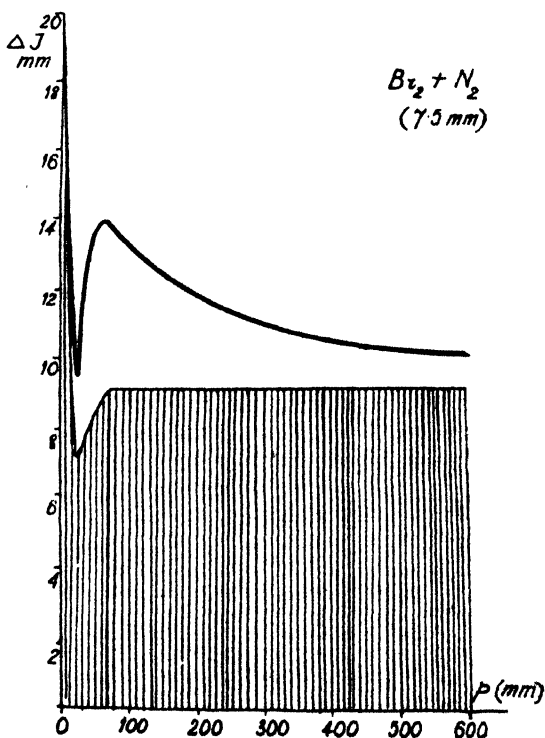


FIG. 3b.—Effects observed in nitrogen, $p_{(\text{Br}_2)} = 4.5 \text{ mm.}$

TABLE I.—*Continued.*

$p(\text{Br}_2)$ mm.	$J \times 10^{-4}$ mm.	$p(X)$ mm.	N_{hv} $\times 10^{-14}$.	ΔJ mm.	$\Delta \times 10^3$.			$C_1 \times 10^{22}$.
					Total.	Therm.	Diss.	

X = Oxygen.

0.290	4.78	94	3.69	13.4	4.62	0.21	4.41	3.31
—	—	143	3.49	11.9	4.10	0.20	3.90	2.62
—	—	246	3.54	8.0	2.78	0.20	2.58	3.52
—	—	351	3.51	7.0	2.52	0.20	2.32	3.04
—	—	465	3.49	5.3	1.83	0.20	1.63	(4.65) 3.66*
								Mean 3.2 ± 0.6

X = Methane.

0.403	4.30	90	4.82	13.1	3.59	0.18	3.41	3.86
—	—	116	4.75	12.4	3.39	0.18	3.21	3.33
—	—	178	4.80	10.8	2.94	0.18	2.76	3.01
—	—	287	4.80	7.9	2.17	0.18	1.99	3.55
—	—	400	4.80	6.5	1.79	0.18	1.61	3.87
								Mean 3.6 ± 0.6

X = Carbon dioxide.

0.280	4.10	81	4.03	11.5	4.45	0.40	4.05	5.28
—	—	105	3.63	9.4	3.62	0.36	3.28	5.58
—	—	145	3.63	8.1	3.12	0.36	2.76	5.71
—	—	196	3.57	6.4	2.47	0.35	2.12	(7.12) 5.12*
—	—	285	3.49	5.1	1.97	0.34	1.63	(8.02) 5.51*
								Mean 5.4 ± 0.5

* Neglecting the thermal effect.

as in the case of iodine,² the results obtained in O_2 above 450 mm. and in CO_2 above 200 mm. indicate that the thermal effect is destroyed at these pressures by convection-currents, as discussed in ⁶.

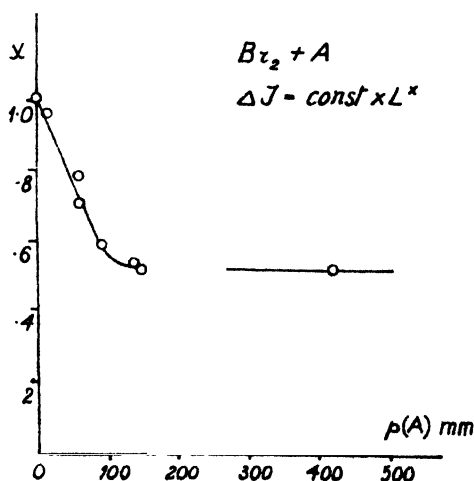


FIG. 4.—Dependence of the effect on light-intensity.

The values of C_1 obtained with bromine are less exact than those obtained with iodine² because the effects are considerably smaller. (The extinction-coefficients $\bar{\alpha}_J$ and $\bar{\alpha}_L$ being much lower for Br_2 than for I_2 .) Considering Table I. we may assume that the C_1 values are correct to about 10 per cent. in the case of He and H_2 , and to 25 per cent. in that of A. We must, however, mention, that the reproducibility of the results, which was very good with iodine, was not so good with bromine. Sometimes, under apparently identical conditions, we found effects 20-40

⁶ E. Rabinowitch, *Z. physik. Chemie (B)*, 1936.

per cent. smaller than those which were used in the calculation of the tables. It appears as if small traces of some unknown substances are able to catalyse the recombination of bromine atoms. In experiments with iodine we found that practically no dissociation-effect can be observed in mixtures of I_2 with water-vapour. It is therefore possible that traces of moisture are responsible for the smaller effects in bromine also. This is, however, a point requiring special investigation.

The results used in Table I. were those in which the highest effects were observed. After a few experiments giving "too small" effects, we were always able to obtain the higher ones again. This was proved especially in the case of helium, where about 20 sets of measurements gave results in accordance with Table I. Table II. which contains a comparison of the recombination constants for bromine and iodine, confirms the reliability of the bromine values by showing their constant relation to the corresponding values for iodine.

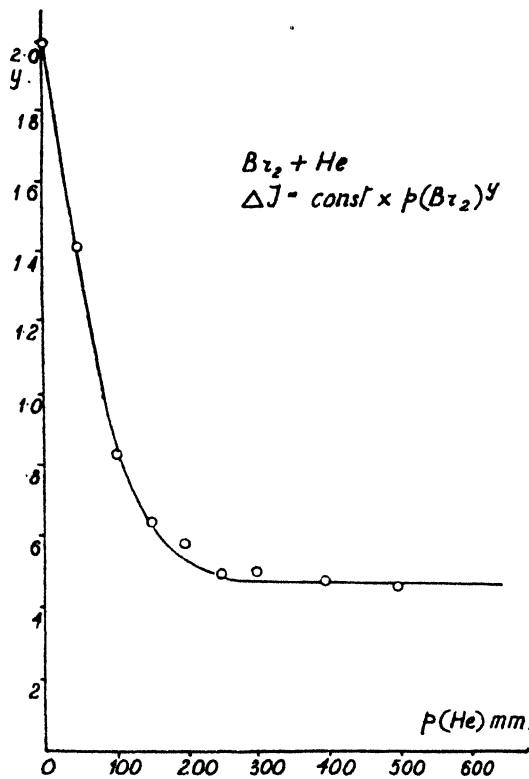


FIG. 5.—Dependence of the effect on bromine-pressure.

TABLE II.—RECOMBINATION-CONSTANTS FOR BROMINE AND IODINE.

X =	H ₂ .	He.	CH ₄ .	N ₂ .	O ₂ .	A.	CO ₂ .	C ₂ H ₆ .
$C_1 \times 10^{32}(\text{Br})$	2.2	0.76	3.0	2.5	3.2	1.3	5.4	—
$C_1 \times 10^{32}(\text{I})$	4.0	1.8	12	6.6	10.5	3.8	18	100
$C_1(\text{Br})/C_1(\text{I})$	0.54	0.42	0.30	0.38	0.30	0.34	0.30	—
$\gamma(\text{Br}) \times 10^3$	2.2	0.82	3.7	2.7	3.4	1.4	5.7	—

The gases are arranged in Table II. in order of their molecular weights, to show that the relation $C_1(\text{Br})/C_1(\text{I})$ is slightly higher for the light gases H₂ and He, and practically constant for all the heavier ones. This suggests that the *velocity* of the molecules has a somewhat greater influence on their efficiency as third bodies in the case of the recombination of bromine atoms.

The last row of Table II. shows the proportion of the total number of

double collisions $\text{Br} + \text{Br}$ which are recombining collisions at atmospheric pressure of the gas X ($t = 20^\circ \text{C.}$). The number of double collisions is calculated by the usual kinetic formula, using the reasonable value 4.5 \AA. for the collision diameter of two Br atoms. One collision in 1200 is a recombining one in helium, and one in 175 in carbon dioxide.

The order of efficiency of different gases in promoting recombination is the same as in the case of iodine. Monoatomic gases have a smaller effect than the polyatomic ones. The efficiency increases with growing molecular size and intensity of the van der Waals' forces of the colliding molecules.

For the comparison of the values of C_1 given in Table II. with those derived by Jost⁷ and Hilferding and Steiner⁸ from the kinetics of the bromine-hydrogen reaction we must refer to a separate note.⁶

V. Effects in Pure Bromine.

As stated above, the effects observed in pure bromine are of thermal origin. It has already been shown (Figs. 4 and 5) that the dependence of the effect in pure Br_2 on light intensity and bromine concentration is in accordance with this theory. We will now show the same for the *absolute magnitude* of the effects.

From formula (1) we derive

$$\frac{\Delta_{\text{therm.}}}{Q} = -\frac{3}{32\kappa_{(\text{Br}_2)}T} = 32 \quad (10)$$

using the values $T = 293^\circ \text{ abs.}$ and $\kappa_{(\text{Br}_2)} = 1.0 \times 10^{-5}$ (for derivation of this value see ¹).

The effects in pure Br_2 vapour are very large at higher pressures; the calculation of Δ and Q is, however, somewhat complicated, the simple formulæ (5) and (6) being valid only for small absorptions. For the calculation of Δ at higher pressures, we determined experimentally the transmission J as a function of $p_{(\text{Br}_2)}$. By differentiating the curve $J = f(p)$ we obtained the values of $dJ/d[\text{Br}_2]$ for different pressures, and were thus able to calculate $\Delta \equiv \frac{\Delta[\text{Br}_2]}{\text{Br}_2}$ from the experimental values of $\Delta J/J$.

For calculating Q , we introduced into (5) a correction (not exceeding 20 per cent.) accounting for the absorption of the L light between the middle of the vessel and the back wall, using the values of \bar{a}_L given in Fig. 1 A.

Fig. 6 shows the values of Δ/Q calculated from a large number of experiments. Circles refer to measurements made with L light filtered through CuSO_4 only (*cf.* Fig. 1), crosses to measurements made with Wratten-filter No. 32 in addition to the CuSO_4 -filter. Filter 32 cuts off all wave-lengths above the convergency limit of Br_2 at 5000 \AA. ; we used it at the beginning of our investigation in order to be sure of the absence of any effects due to *excitation* of Br_2 molecules. The numerical coefficient in equation (5) is 3.10 for the light filtered through filter No. 32.

Fig. 6 shows that the values of Δ/Q are practically constant at pressures above 11 mm. The mean value is 35, which is remarkably close to the theoretical value 32 (shown by the thick line). A better agreement cannot be expected on account of the idealisations used in the theoretical treatment. An endless cylindrical vessel $r = 1 \text{ cm.}$, was considered in

⁷ W. Jost, *Z. physik. Chemie (B)*, 1929, **3**, 83, 95.

⁸ K. Hilferding, W. Steiner, *ibid.*, 1935, **30**, 399.

the derivation of (1), whereas the actual experiments were made partly in a cylindrical vessel $r = 1$ cm., $d = 10$ cm., partly in a rectangular cell $2 \times 2 \times 12$ cm.

This result proves the essential correctness of the theory of the thermal effect, especially the assumption that convection can be neglected in calculating the stationary state of the illuminated gas (at least in the case of pure Br_2 vapour at pressures up to about 20 mm.).

Below $p(\text{Br}_2) = 11$ mm., the values of Δ/Q decrease. We predicted¹ that an effect of this kind must occur: it is due to the transition from the region of homogeneous recombination into that of predominant wall-recombination. The bending of the curve at $p = 11$ mm. in Fig. 6 has thus the same meaning as the maxima in Figs 2 and 3. The decrease in the thermal effect at pressures below this point is caused by the walls ab-

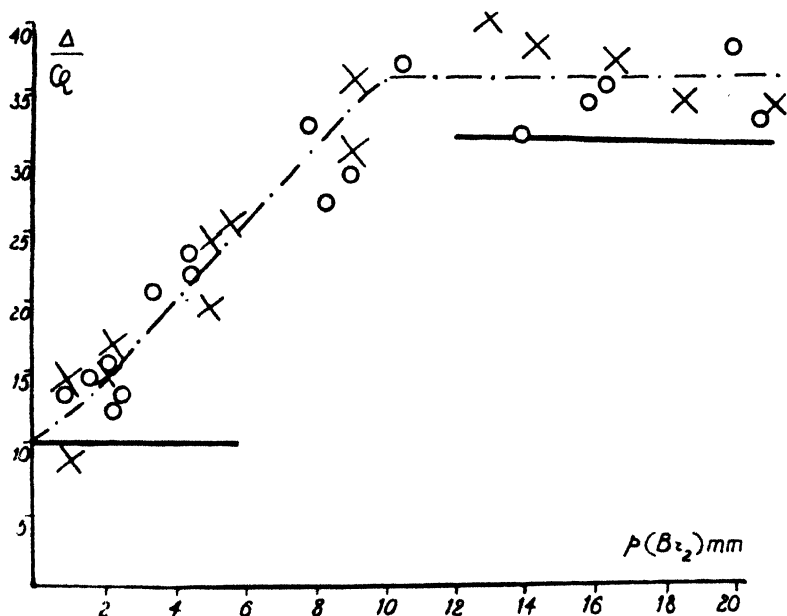


FIG. 6.—Dependence of the effect in pure bromine on pressure.

sorbing the recombination energy of the atoms. In the extreme case of purely heterogeneous recombination the whole of the dissociation energy is conveyed to the walls. The thermal effect does not, however, disappear completely. This result was also predicted¹ as a consequence of the fact that the light-quanta absorbed are greater than those required for the bare dissociation of Br_2 into two normal Br atoms. The excess energy is converted partly into the excitation energy of the one Br atom, and partly into kinetic energy of the atoms. With a mean wave-length 4330 Å., this excess energy Q' is

$$Q' = \frac{6300 - 4330}{6300} Q = 0.31 Q \quad . \quad . \quad . \quad (11)$$

(6300 Å. being the wave-length corresponding to the dissociation energy of Br_2). The corresponding value of Δ/Q is $0.31 \times 32 = 10$, and Fig. 6 shows that this is, in fact, the value Δ/Q approaches at low bromine-pressures.

The number of double collisions which a Br atom suffers on its way to the wall (*i.e.* on a diffusion-path of the order of 1 cm.) under a pressure of 1 mm. can be roughly estimated as being of the order of 10^5 (the diffusion-coefficient of Br atoms into Br₂ assumed to be of the order of 0.05). This gives an upper limit for the stability of the metastable 2P_1 state of Br for collisions with Br₂ molecules.

The curve $\Delta/Q = f(p)$ shifts towards higher pressures at lower light intensities, in the same way as was found for the curves of the dissociation effect.² Fig. 7 shows Δ/Q as a function of L at three different pressures. At sufficiently high L values, the limiting value 35 is already attained at pressures below 11 mm. At sufficiently low L values, Δ/Q drops below 35 even at a pressure as high as 16.4 mm.

The position of the "transition point" in pure bromine ($p = 11$ mm.) can be compared with that found in other gases (for instance $p = 75$ mm.

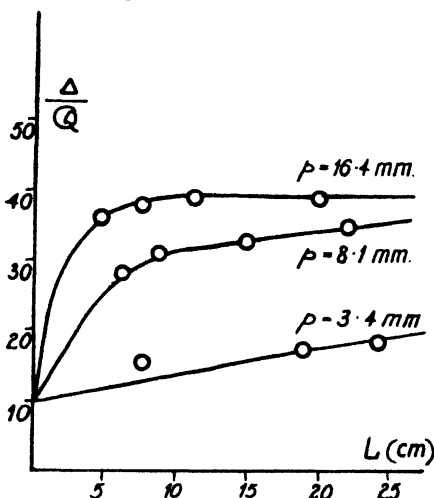


FIG. 7.—Dependence of the effect in pure bromine on light-intensity.

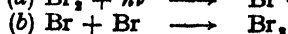
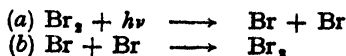
in CH₄ and CO₂). It gives an indication of the great velocity of homogeneous recombination of Br-atoms with Br₂ as third body. Unfortunately the position of this point depends not only on the value of C_1 , but (as shown by Figs. 2 and 3) also on the diffusion-coefficient of the atoms (which determines the slope of the ascending part of the curves). All we can say about the value of C_1 for Br₂, therefore is, that it must be sensibly larger than the corresponding constant for CO₂—probably not smaller than 20×10^{-23} .

The effects discussed in this section bear a close connection to the so-called "Budde effect"

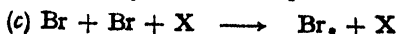
(increase in pressure of illuminated halogen vapours) which has been the object of a great number of investigations. Most of them have been carried out under conditions which make a theoretical treatment impossible, (inhomogeneous absorption, complicated shape of the vessel, convection-currents, etc.). The experiments discussed above show that, if suitably simple conditions are chosen, this effect is susceptible of simple theoretical discussion and may be used to provide information concerning the mechanism of conversion of light energy into heat, heat transport, and heat exchange with the walls in different gases.

Summary.

The stationary state of dissociation of illuminated Br₂ vapour



has been measured by an optical method described previously^{1, 2, 3}. The thermal effects were practically suppressed by using a sufficiently low bromine pressure. The velocity constants C_1 of the reactions



have been determined for a number of different gases X. (He, A, H₂, N₂, O₂, CH₄ and CO₂.) The results are given in Table II. The recombination-velocity of Br atoms is 2 to 3 times smaller than that of the iodine atoms with the same "third body" X. One collision Br + Br in 1100 is a recombining one in He at atmospheric pressure, 1 in 175 in CO₂, etc.

The dependence of the degree of dissociation on light intensity, bromine concentration and pressure of the gas X is in agreement with the theory of the "three body recombination." Br₂ or other complexes play no rôle in the recombination process. Indications were found of some substances (H₂O ?) catalysing the recombination process.

The effects observed in pure illuminated Br₂-vapour were also investigated and found to be in quantitative agreement with the theory of the thermal effect.

Our heartiest thanks are due to Prof. F. G. Donnan, F.R.S., for his interest and encouragement in the course of this work, and for the hospitality he gave us in the Sir William Ramsay Laboratories.

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THE HETEROGENEOUS RECOMBINATION AND THE DIFFUSION COEFFICIENTS OF HALOGEN-ATOMS.

BY E. RABINOWITCH AND W. C. WOOD.

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At sufficiently low pressures the recombination of photochemically produced atoms of Br or I takes place mainly on the walls of the vessel.^{1, 2, 3} The resulting stationary distribution of atoms and molecules was discussed in¹ for the simple case of a uniformly illuminated, infinitely long cylindrical vessel of a radius $R = 1$ cm. The following equation was derived for the mean stationary decrease in the concentration of Hal₂ molecules in the central part of the vessel ($r = 0.5$ cm.).

$$\Delta[\text{Hal}_2] = \frac{5}{16} \frac{p_{\text{atm.}}(\text{X})N_{\text{h}}}{D_0} \quad (1)$$

N_{h} is the number of quanta absorbed per sec. in 1 c.c., $p_{\text{atm.}}(\text{X})$ the pressure of the gas X (= He, H₂ . . .) filling the vessel and D_0 the coefficient of diffusion of the halogen-atoms into the gas X under atmospheric pressure. The concentration-change $\Delta[\text{Hal}_2]$ was measured by means of an optical arrangement, described elsewhere.^{1, 2}

Formula (1) requires a proportionality of the observed effect with the light intensity and with the pressure of the gas X. These laws in fact hold at sufficiently low pressures, as discussed^{2, 3} and shown, for instance, in Fig. 1 for the case of iodine and helium.

¹ E. Rabinowitch, H. L. Lehmann, *Trans. Faraday Soc.*, 1935, **31**, 689.

² E. Rabinowitch, W. C. Wood, *J. Chem. Physics*, 1936.

The coefficient $\frac{\Delta J}{l}$ in (1) is based on the above-mentioned idealisation of the geometrical conditions—the actual reaction vessel was a rectangular one, $12 \times 2 \times 2$ cm. In observing the thermal effects, which occur under analogous conditions in pure bromine-vapour, we found³ that the numerical coefficient in a formula derived under the same assumptions was not in error by more than 10 per cent. We may therefore assume the same for the factor $\frac{\Delta J}{l}$ in (1). The same experiments showed that at sufficiently low pressures the convection-currents play no rôle in conducting to the walls the energy absorbed in the body

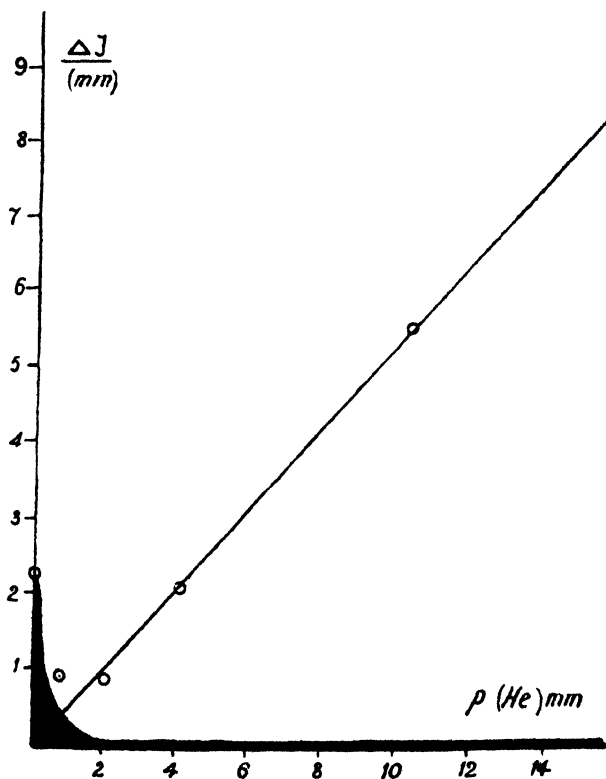


FIG. 1.

of the gas. We are therefore entitled to assume that the migration of the atoms to the walls also occurs solely by diffusion. These assumptions permit us to calculate, by equation (1), the diffusion-coefficient D_0 from the experimental values of $\Delta[\text{Hal}_2]$ found at low pressures of the gas X.

Tables I. and II. contain the experimental data. N_{hal} is calculated from L and $\rho[\text{Hal}_2]$ by means of equations (4),^{2,3}

$\Delta[\text{Hal}_2]$ from ΔJ and J by means of equations (1)² and (6).³ This

gives us the equations above the tables permitting a calculation of D_0 directly from the experimental data. The "most probable" D_0 -values are in most cases those found at the lowest pressures and the smallest light-intensities, because under these circumstances the influence of the homogeneous recombination is smallest.

Table III. gives the comparison of the D_0 -values found for the diffusion of Br and I into different gases X.

The value for CO_2/Br_2 is an upper limit only, because 23 mm. is not a sufficiently low pressure for this gas.

The order of magnitude and the relative values of D_0 found for different gases X are all very plausible, thus showing the essential correctness of the mechanism assumed. It is, however, unexpected to find the

³ E. Rabinowitch, W. C. Wood, *This vol.*, 1936 (preceding paper).

diffusion-coefficients of the Br-atoms about 25 per cent. smaller than those of the I atoms; the inverse relation would appear more likely in view of the relative masses and diameters of the atoms.

Fig. 2 shows the known diffusion-coefficients of monoatomic gases as a function of their position in the periodic system. The values given in Table III. for the I atoms are in agreement with an interpolation for

TABLE I.—DIFFUSION COEFFICIENTS OF IODINE-ATOMS.

$$D_0 = 9.6 \times 10^{-7} \times L p_{\text{mm.}}(X) \times p_{\text{mm.}}(I_2) \left(\frac{J}{\Delta J} \right).$$

X.	$p(I_2)$, mm.	$J \times 10^4$, mm.	$p(X)$, mm.	L , cm.	ΔJ , mm.	D_0 .	Most Probable Value.
H ₂	0.128	3.97	50 50	72 35	28 13.5	0.63 0.63	0.6
He	0.136	3.89	54 54	59 27.5	26 13.5	0.63 0.56	0.6
	0.150	3.82	4.1 10.5	67 72	2.2 5.5	0.70 0.77	
			10.5 19.6	32 68	3.0 10.3	0.64 0.73	
			34	69	17.7	0.76	
A	0.140	4.42	22 22	73 34	55 30	0.19 0.16	0.16
N ₂	0.141	5.03	13 13 26	66 31 66	39 19.5 58	0.15 0.14 0.20	0.14
				31	31.5	0.17	
O ₂	0.142	3.90	22	58 26.5	27 14	0.25 0.22	0.18
	0.141	4.81	17	67 33	39 21	0.20 0.18	
CH ₄	0.160	4.47	17 31	64.5 30 61.5	37 21 57	0.20 0.17 0.26	0.17
				29.5	29	0.20	
	0.153	4.16	20	79 38	42.5 23	0.22 0.21	
CO ₂	0.141	4.66	14	67 31	47 23	0.12 0.11	0.11
C ₆ H ₆	0.150	4.61	3.1	60	30	0.04	0.04

a monoatomic gas in the fifth period; those found for the Br atoms are rather too small for their position in the fourth period.

The D_0 values of I are more exact than those found for Br, because derived from much larger effects. It is, however, improbable, that all ΔJ -values used for Br₂ are in error by as much as 50 per cent.

A possible explanation of the experimental results which does not assume that the diffusion-coefficients of bromine-atoms are smaller than those of iodine-atoms is the following. In deriving equation (1),

920 DIFFUSION COEFFICIENTS OF HALOGEN-ATOMS

we assumed the concentration of the atoms in the immediate neighbourhood of the walls to be zero. If we put the concentration of atoms at the wall equal to some constant value $[\text{Br}]_0 \neq 0$, we obtain, instead of (1), the equation

$$\Delta[\text{Br}_2] - \frac{1}{2}[\text{Br}]_0 = \frac{5}{16} \frac{p_{\text{atm.}}(\text{X})N_{\text{Av}}}{D_0} \quad (2)$$

The same value of $\Delta[\text{Br}_2]$ now corresponds to a higher value of D_0 .

TABLE II.—DIFFUSION-COEFFICIENTS OF BROMINE ATOMS.

$$D_0 = 4.6 \times 10^{-8} L p_{\text{mm.}}(\text{X}) \times p_{\text{mm.}}(\text{Br}_2) \left(\frac{J}{\Delta J} \right).$$

X.	$p(\text{Br}_2)$, mm.	$J \times 10^4$.	$p(\text{X})$, mm.	L , cm.	ΔJ , mm.	D_0 .	Most Probable Value.
H_2	0.312	5.13	18	58	2.5	0.35	0.5
			72	58	5.9	0.59	
	0.525	3.68	47	64	6.6	0.45	
He	0.79	3.36	36	63	9.1	0.34	0.4
	0.30	4.15	41	70	11.2	0.42	
A	0.29	4.39	31	55.5	16.2	0.08	0.11
	0.41	4.23	28	62	12.8	0.12	
	0.34	3.96	17	65	7.6	0.10	
			43	65	11	0.17	
	0.32	4.02	10	68	4.7	0.09	
			27	63	10.6	0.11	
N_2	0.38	3.62	17	67.5	7.1	0.12	0.12
O_2	0.515	3.98	12	70	68	0.13	0.13
CH_4	0.40	4.37	15	67	8.2	0.11	0.11
CO_2	0.335	3.80	23	79	8.8	<0.13	<0.13

TABLE III.—DIFFUSION-COEFFICIENTS.

X =	H_2 .	He.	N_2 .	A.	O_2 .	CH_4 .	CO_2 .	C_6H_6 .
Br-atoms	0.5	0.4	0.12	0.11	0.13	0.11	(0.13)	—
I-atoms	0.6	0.6	0.14	0.16	0.18	0.17	0.11	0.04
$\frac{D_0(\text{Br})}{D_0(\text{I})}$	0.8	0.7	0.8	0.7	0.7	0.6	—	—

The recombination of the atoms takes place in the following way: The atoms are adsorbed; they move on the surface of the wall as a two-dimensional gas and recombine by collisions. In the stationary state the concentration of the atoms on the surface must be high enough to make the rate of recombination equal to the rate of production of atoms in the gas. In our experiments 10^{17} atoms were produced per second in the whole vessel (50 c.c.); they had to recombine on a surface of 100 sq. cm., thus requiring a rate of 10^{15} atoms per second per sq. cm.

If we assume the adsorbed atoms to be freely moving about, the total collision-number per second at a concentration $[\text{Hal}]_{\text{ads}}$ will be

$$Z_{\text{abs.}} = 2\sqrt{\frac{RT}{M}} [\text{Hal}]_{\text{abs.}}^2 \sigma \quad (3)$$

With σ (the molecular diameter) = 4.5 Å., $M = 80$ and $T = 293^\circ \text{ abs.}$, we obtain

$$Z = 10^{-3} [\text{Hal}]_{\text{ads.}}^2.$$

The concentration necessary to give $Z = 10^{15}$ is

$$[\text{Hal}] = 10^9 \text{ atoms/cm.}^2.$$

This is a very small fraction of a complete layer and it is improbable that it gives rise to a vapour pressure of the order of 1×10^{-4} mm. (which

is the partial pressure of the Hal-atoms in the centre of the vessel). It is, however, conceivable that, because of some restriction of the free motion of the atoms on the surface, the stationary concentration of the atoms in the adsorbed phase is much higher than 10^9 . The fact that the greater part of the surface is covered with adsorbed Hal_2 molecules also increases the relative saturation of the surface with atoms. These two causes may result in the vapour pressure of adsorbed Hal-atoms becoming in fact of the same order as their pressure in the centre of the vessel. It is reasonable that this may occur with

Br-atoms although not with I-atoms, because the energy of adsorption of the former is probably much smaller.

We may thus suppose, that whereas the diffusion-coefficients given in Table III. for iodine are correct, the values calculated for bromine may be somewhat too small because of the neglect of the term $\frac{1}{2}[\text{Br}]_0$ in equation (2).

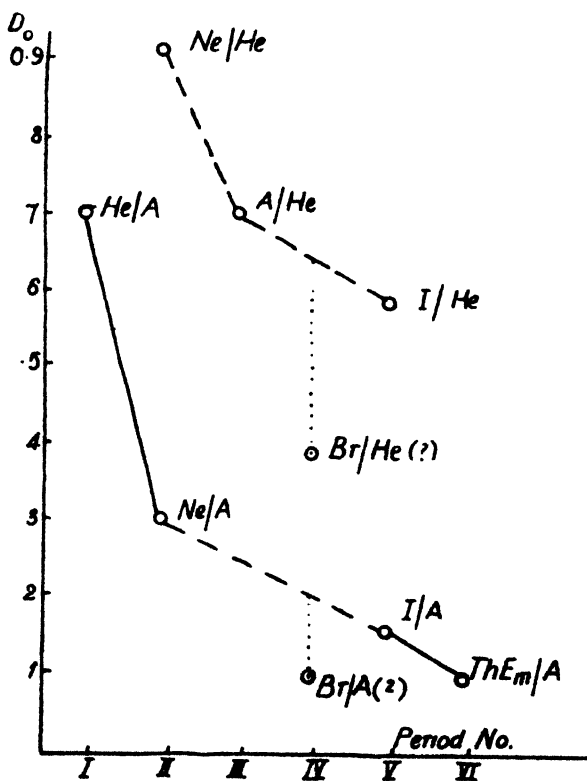


FIG. 2.

Note added in Proof.—Bodenstein and Winter have just published in *Sitzungs-berichte* a paper concerning the $\text{H}_2 - \text{Cl}_2$ reaction in which they

suggest that the stationary concentration of Cl atoms in an illuminated gas may be practically uniform throughout the vessel (instead of dropping to zero near the surface of the walls). This result is obviously in agreement with the idea we here put forward; it is reasonable to expect adsorbed Cl atoms to have a vapour pressure even higher than that of the adsorbed Br atoms. We do not, however, agree with Bodenstein and Winter in deducing that the "accommodation coefficient" of Cl atoms *must* be much less than unity. The important factor is the equilibrium-concentration of the atoms in the gas phase which may differ from zero, even if every atom striking the walls becomes adsorbed, so long as the velocity of desorption is sufficiently high.

Summary.

The diffusion-coefficients of the free atoms Br and I into different gases (He, A, N₂, H₂, O₂, CH₄, CO₂) are calculated from measurements of the stationary dissociation of illuminated halogen vapours at low pressures.

Our heartiest thanks are due to the Director of the Laboratories, Professor F. G. Donnan, F.R.S., for hospitality and encouragement he gave us.

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THE MECHANISM OF THE CATALYTIC EXCHANGE REACTION BETWEEN DEUTERIUM AND WATER.

BY ADALBERT FARKAS.

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The catalytic exchange of hydrogen and deuterium atoms between liquid water and heavy hydrogen, $\text{HD} + \text{H}_2\text{O} \rightleftharpoons \text{HDO} + \text{H}_2$, was discovered¹ and fully investigated by Horiuti and Polanyi.² According to these authors this reaction involves the ionisation of the hydrogen or deuterium molecules on the catalyst (Pd, Pt or Ni).

The subject of the present paper is the investigation of the catalytic exchange reaction in the gaseous phase on a hot platinum wire.³

1. Experimental.

The experimental arrangement was similar to that used in the investigation of the catalytic interaction of deuterium and ammonia.⁴ A platinum wire (50 cm. long and 0.1 mm. in diameter) mounted in the

¹ J. Horiuti and M. Polanyi, *Nature*, 1933, **132**, 819.

² J. Horiuti and M. Polanyi, *Mem. Proc. Manchester Lit. Phil. Soc.*, 1934, **78**, 47.

³ For an application of this reaction for a method of analysis of heavy water, see A. Farkas, *Trans. Faraday Soc.*, 1936, **32**, 413.

⁴ Cf. A. Farkas, *ibid.*, 416.

reaction tube as shown in Fig. 1 was used as catalyst, its temperature being regulated in the usual way by electric heating (Series I.) (resistance of the wire at 15° C. 35.4 ohms) or by heating the whole reaction vessel in a small electric furnace (Series II.). Whilst the two methods give concordant results so far as the progress of the reaction with time and its dependence on pressure are concerned, the dependence of the reaction rate on temperature was more accurately determined by the latter method since then every possibility of a non-uniform temperature distribution (due to end-losses and other causes⁵) is excluded. If not otherwise stated the experiments were carried out by this method. About 1 c.c. of water was placed either in the U-tube (see Fig. 1) or at the bottom of the reaction tube which protruded from the furnace and was kept at constant temperature. Thus the reaction vessel always contained the vapour corresponding to the actual temperature of the water.

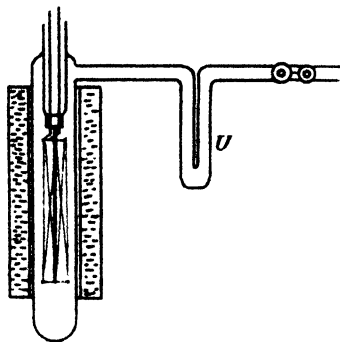


FIG. 1.

The experiments were carried out as follows: an amount (usually 15 mm. Hg) of heavy hydrogen (60-100 per cent. D) was added to the water vapour present in the reaction vessel, the filament or the whole vessel heated to the given temperature; from time to time small samples of gas were withdrawn from the tube by means of the capillary lock and the D-content analysed by the micro-conductivity method.⁶ In all experi-

ments care was taken to ensure a complete mixing of the gases, *i.e.*, to avoid any differences in the D-content of the hydrogen in the vessel and in that of the hydrogen near the lock, and also to avoid any inhibition of the exchange reaction by lack of a sufficient rate of diffusion of the water vapour to and from the liquid water. Since both liquid water and vapour were always present in very large excess the equilibrium in the exchange reaction was established when practically all the deuterium has disappeared from the heavy hydrogen originally added.

TABLE I.

12 mm. H₂O. 12 mm. D₂ (88 per cent. D)
(Expt. II. 17).

Time in Minutes (t).	Per Cent. D.	$k = 1/t \ln D_0/D.$
0	88	—
30	67.5	0.00882
45	57.5	0.00940
71	47	0.00875
94	38	0.00864
217	12	0.00915
		Mean 0.00895

The catalytic activity of the platinum wire was quite reproducible in a series of experiments carried out during the same day, but changed somewhat in the course of a few weeks. Thus care was taken to ascertain that no change had taken place in the activity of the catalyst when, *e.g.*, the dependence of the reaction rate on temperature or pressure was being investigated.

To obtain some information about the state of the hydrogen in the adsorbed layer, in addition to the exchange reaction, the conversion of *parahydrogen* and *orthodeuterium* was investigated in a way similar to that employed in the catalytic interaction of deuterium and ammonia. This proved to be an excellent tool in investigating the surface properties of the catalyst.

⁵ A. Farkas and H. H. Rowley, *Z. physik. Chemie, B.*, 1933, **22**, 335.

⁶ A. and L. Farkas, *Proc. Roy. Soc., A.*, 1934, **144**, 467.

2. Dependence of the Reaction Rate on Temperature.

The progress of the exchange reaction with time is shown in Table I. at 236°. It will be noted that the progress of the exchange reaction is well represented by the expression

$$(D) = (D_0)e^{-kt}$$

(*D*) and (*D*₀) denoting the percentage of *D* contained in the heavy hydrogen at time *t*, and *t* = 0 respectively), as shown by the constancy of *k*.

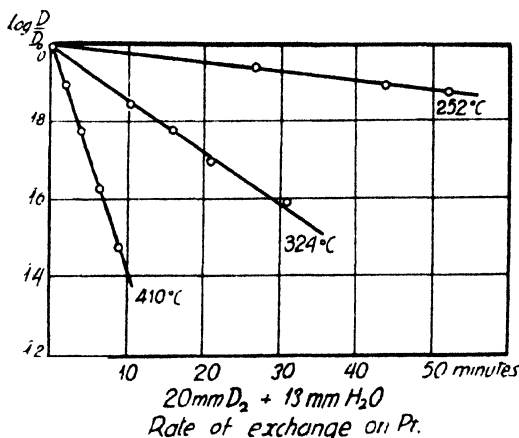


FIG. 2.

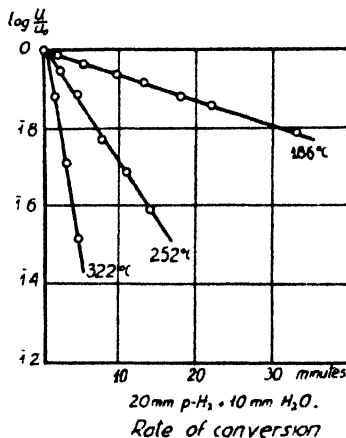


FIG. 3.

Fig. 2 shows the progress of the exchange reaction in a mixture similar to that above in the temperature region 252–410° C., $\log D/D_0$ being plotted against time. The temperature 410° C. was obtained by heating the wire electrically, while the reaction vessel itself was kept at 330° C.

In fig. 3 similar lines are shown for the rate of the conversion of *p*-H₂ in the presence of water vapour, $\log u/u_0$ being plotted against *t* (*u* =

TABLE II.

(Expt. No. 20. 13 mm. *o*-D₂ + 12 mm. H₂O. 327° K.)

Time in Minutes.	Ω in ohms.	$\Delta\Omega$ in ohms.	Per Cent. D.	Per Cent. <i>o</i> -D ₂ in Excess (Relative).
0	13.6	2.54	100	100
3	12.3	1.30	87.5	66
6	11.5	0.72	80.5	43
11	11.0	0.38	75.5	26
24	9.2	—	62.0	—
33	8.5	—	56.0	—
42	7.6	—	50.0	—
60	6.3	—	41.0	—

excess concentr. of *p*-H₂). It will be seen that at the same pressure and temperature the *para*hydrogen conversion proceeds about 8–10 times more quickly than the exchange.

Similar results were found if the vessel was kept cold and only the platinum wire was heated electrically. One experiment prob-

ably deserves mentioning in which the *ortho*-*para*-hydrogen conversion and the exchange reactions are investigated simultaneously in the same gas mixture.⁴ In this experiment 13 mm. *ortho*-D₂ were added to 12 mm. of water vapour. The resistance value of this *o*-D₂ as determined according to the microthermoconductivity method is 2.54 ohms higher than that of normal D₂, into which it can be reconverted by passing it over a hot nickel filament.⁵ Thus the resistance value of each sample withdrawn from the reaction tube was determined, first directly, then after having passed the

nickel filament: the latter value giving the percentage D, the difference between the former and the latter ($\Delta\Omega$) the amount of *ortho*-D₂ in excess relative to normal D₂. Table II. shows the results obtained. The figures listed in column 2 under heading Ω represent the additional resistance value of the sample compared with normal H₂.

In evaluating the figures listed in column 3 one had to take into account that with the percentage of D the percentage of the molecules D₂ also decreases. Since per cent. D₂ = (per cent. D)²/100, the figures in column 5 were obtained from

$$\frac{\Delta\Omega \times 100}{2.54 \times \text{per cent. D}_2} \times 100.$$

The actual per cent. *o*-D₂ is obtained by adding one-third of these figures to 66 per cent. which is the percentage of *o*-D₂ in normal deuteriums. From this table it is evident that whereas the *ortho*-D₂ content has decreased in 5 minutes to half of its original value the D-content decreases by the same amount in 42 minutes, i.e. the ratio of the velocities for these two reactions is again 8:1.

In a third series (the catalyst having slightly higher activity than in experiments shown in Fig. 2) the rate of the *parahydrogen* conversion was investigated in the absence of water vapour the U-tube containing the water being kept at the temperature of liquid air. The results obtained are summarised in Table III. together with the data represented graphically in Figs. 2 and 3, the reaction velocity being characterised by the half-life time $\tau = \ln_2/k$. The activation energies listed in column 4 were calculated in the usual way according to Arrhenius' formula.

It is evident that in the presence of water vapour the *parahydrogen* conversion appears to be inhibited and its energy of activation considerably increased.

3. Dependence of the Reaction Rate on Pressure.

Both the rate of the exchange reaction and the rate of the *parahydrogen* conversion have been investigated in respect to their dependence on the water vapour pressure and hydrogen or deuterium pressure. Some typical results are summarised in Tables IV. to VII.

These results indicate: The absolute rate of the exchange reaction (i.e., the number of D-atoms exchanged) being proportional to the expression pressure/ τ (cf. column 4, Tables V. and VII.) increases somewhat less than linearly with increasing deuterium pressure but is practically independent of the water pressure. (The slight decrease in velocity with decreasing H₂O pressure might be due to lack of sufficient speed of diffusion between the reaction vessel itself and the U-tube containing the liquid

TABLE III.

No.	°C.	Half-life Time (τ) in Minutes.	Energy of Activation in Kg cals.
Parahydrogen conversion (20 mm.) in the absence of water vapour.			
II 11	142	9.5	6.4
II 10	182	4.8	
II 9	217	3	
Parahydrogen conversion (20 mm.) in the presence of (10 mm.) water vapour.			
II 23	186	45	10.8
II 22	252	10	
II 21	322	2.5	
Exchange reaction 20 mm. D₂ + 10 mm. H₂O.			
II 31	252	120	13.5
II 30	324	21	
II 32	410	5.2	
II 31a	535	2	

TABLE IV.—DEPENDENCE OF EXCHANGE ON THE H_2O PRESSURE. D_2 PRESSURE = 20 mm.

No.	Temperature °C.	H_2O Pressure in mm.	Half-life (τ) in Minutes.
II 27	322	1	32
II 26	325	4.5	34
II 25	326	10	23
II 33	410	4.5	8
II 32	410	13	5.2
II 34	410	17	6

TABLE V.—DEPENDENCE OF EXCHANGE ON THE DEUTERIUM PRESSURE. TEMPERATURE $296^\circ C$. H_2O PRESSURE = 11 mm. (WIRE HEATED ELECTRICALLY.)

No.	Deuterium Pressure in mm.	Half-life (τ) in Minutes.	P_{D_2}/τ
I 24	10	25	0.4
I 23	24	28	0.86
I 22	55	35	1.58

TABLE VI.—DEPENDENCE OF THE RATE OF *Para*-HYDROGEN-CONVERSION ON THE H_2O PRESSURE. $p-H_2$ PRESSURE = 20 mm.

No.	Temperature °C.	Water Pressure in mm.	Half-life in Minutes.	Relative Velocity.
II 14	140	0	20	1.00
II 13	142	5	75	0.27
II 6	218	0	2.0	1.00
II 7	218	5	4.5	0.45
II 8	218	16	8.4	0.24
II 9	218	0	3.0	—
II 29	244	0	2.6	1.00
II 28	248	0.4	3.4	0.67

TABLE VII.—DEPENDENCE OF THE RATE OF THE *Para*HYDROGEN CONVERSION ON THE HYDROGEN PRESSURE. TEMPERATURE = $254^\circ C$. H_2O PRESSURE = 12 mm. (WIRE HEATED ELECTRICALLY.)

No.	$p-H_2$ Pressure in mm.	Half-life in Minutes.	Pressure/ τ .
I 18	7	5.5	1.27
I 14	14	5.6	2.50
I 17	35	6.5	5.4

water.) On the other hand, the absolute rate of the *parahydrogen* conversion is proportional to the *parahydrogen* pressure, but is strongly inhibited by the presence of water vapour. The inhibition is the more marked the lower the temperature, *e.g.*, at $140^\circ C$. 5 mm. of H_2O is enough to cut down the velocity of the conversion to nearly one quarter. This inhibition by water is reversible, *i.e.*, the original activity is recovered as soon as the water is removed (*cf.* Table VI.).

4. Dependence of the Reaction Rate on the Treatment of the Catalyst.

In the experiments so far described the catalyst was not specially treated, and it was found that in the temperature region investigated the activity for the conversion reaction in absence and presence of water and for the exchange reaction was fairly reproducible.

In the following experiments the activity of the platinum wire was measured by the catalysis of the *parahydrogen* conversion in the absence of water vapour (U-tube kept at liquid air temperature, *cf.* Fig. 1). It was found that by glowing the wire *in vacuo* its activity was increased manifold, and water vapour had an extremely strong poisoning effect apart from its reversible inhibition already described (*cf.* Table VI.). On the other hand, addition of air did not influence the activity.

The wire in its active form caused a considerable p -H₂ conversion even at lower temperatures. The rate of the conversion was again not altered by bringing the wire into contact with a few millimetres of air⁷ but was cut down to less than a tenth by adding and removing 0.1 mm. of water vapour (*cf.* Table IX.).

The highly active form of the wire could be also obtained by heating the wire in hydrogen to temperatures above 300° C. as shown by the following experiment. After the wire has been in contact with H₂O vapour the conversion was measured at 238° C. and a half-life of 2.7 mins. The reaction proceeded strictly according to

TABLE VIII.—132° C. PRESSURE 15-20 mm. p -H₂ (WATER VAPOUR ABSENT IF NOT OTHERWISE STATED).

No.	Treatment.	Half-life of Conversion in Minutes.
II 35	Wire after contact with water vapour	30
II 36	Glowed <i>in vacuo</i>	0.5
II 37	4.5 mm. H ₂ O added	63
II 38	Water frozen out	20
II 39	Glowed <i>in vacuo</i>	3.2
II 40	Glowed <i>in vacuo</i>	0.5
II 41	Air added and removed	0.8

the exponential law (*cf.* Fig. 3) showing that during the reaction time no change of the activity has occurred. The following experiment was

TABLE IX.

No.	Treatment.	°C.	Half-life of Conversion in Minutes.
II 42	Wire active	{ 22 86	20
II 43	Contact with air	98	3
II 44	Contact with 0.1 mm. H ₂ O	98	1.1
			13

carried out at 326° C. when a very quick reaction (half-life less than half a minute) was observed. On lowering the temperature to 244° C. the reaction proceeded at least 10 times faster than in the preceding

run, and even at 30° C. with a speed corresponding to a half-life time of 40 mins.

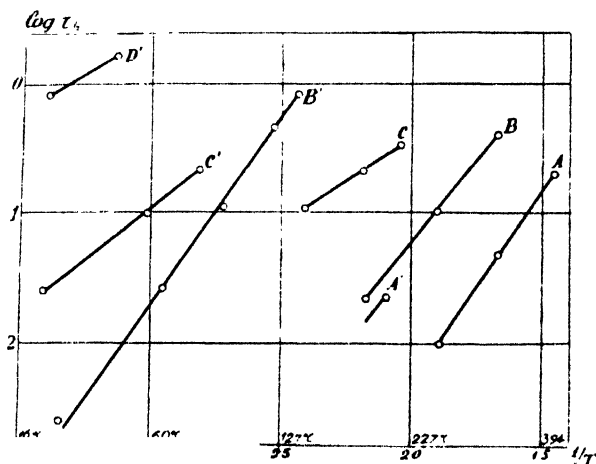
TABLE X.

No.	Remarks.	°C.	Half-life of Conversion in Minutes.	Activation Energy in kg. Cals.
II 64a	(a) 4.5 mm. H ₂ O	25	400	13.7
II 66a	" "	64	38	
II 66b	" "	94	9	
II 63	" "	122	2.2	
II 65	" "	136	1.2	
II 69b	(b) Water frozen out	20	40	6.4
II 69a	" "	59	10	
II 68	" "	82	4.6	
II 70	" "	143	0.4	
II 72	(c) Wire heated in H ₂	21	1.2	5.6
II 73	" "	46	0.6	
II 74	0.01 mm. H ₂ O added	44	4.4	

The poisoning by contact with water vapour and activating by flashing the wire *in vacuo* or heating in H₂ could be reproduced several times.

⁷ K. F. Bonhoeffer and A. Farkas, *Z. physik. Chemie, B.*, 1931, 12, 231.

Actually it was found that by such an alternating treatment the wire became more and more active. With the wire in its most active form in



Temperature dependence of—

- (A) The exchange reaction.
- (B) The p - H_2 conversion in the presence of water vapour.
- (C) The p - H_2 conversion in the absence of water vapour.
- (D) The p - H_2 conversion on the flashed wire.

The letters with dash refer to experiments with the wire in its most active form.

FIG. 4.

grease or mercury was completely excluded. It is probably worth while pointing out the relatively strong poisoning effect of even such minute quantities of water and the large factor of 400 which separates the velocity

in three separate runs the temperature dependence of the rate of the *parahydrogen* conversion at 16-20 mm. pressure was redetermined, (a) in the presence of 4.5 mm. water vapour; (b) after having frozen out the water vapour; (c) after having heated the wire in H_2 to $320^\circ C$. The results are listed in Table X.

Since in the last experiment the water was added by "warming" the U-tube with the water (or rather ice) from liquid air temperatures to $-55^\circ C$. any possibility of the wire being poisoned by impurities such as

Adsorption (in arbitrary units) on Pt.

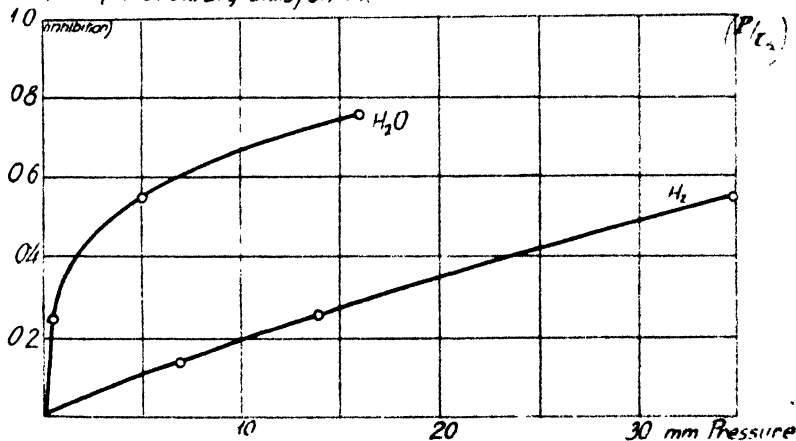


FIG. 5.

at room temperatures on the active wire from the speed in the presence of 4.5 mm. water vapour.

The data of Tables III. and X. are shown graphically on Fig. 4, the logarithms of the half-life times being plotted in the usual way against the reciprocal absolute temperature. It will be noticed that though the

absolute velocities vary in the two sets by a factor of 100 the corresponding lines are more or less parallel as is also indicated by the activation energies.

For the sake of comparison one run of the exchange reaction was also made on the wire in its most active form. At 204° C. and 12 mm. H₂O + 24 mm. deuterium (87 per cent. D) the half-life was found to be 45 minutes (point A' in Fig. 4), i.e., the exchange was proceeding about 10 times more quickly than in the experiments listed in Table III.

5. Exchange Reaction with Liquid Water.

In two additional experiments carried out at 20° C. the rate of the *ortho-para* conversion was compared with that of the exchange reaction involving liquid water according to the same technique as described on page 924.

In one case the exchange reaction between 80 per cent. D₂O (containing N/5 sodium hydroxide) and *parahydrogen* (20 mm.) was investigated, platinum black being used as catalyst. In the other case a suspension of *B. coli* * in ordinary water was brought into contact with *o*-D₂ and the enzymatic catalysis of the exchange reaction was followed up. The results listed in Tables XI. and XII. in the last column again indicate the relative percentage of the *p*-H₂ or *o*-D₂ in excess in the same sense as in Table II. With platinum as catalyst the conversion proceeds definitely more slowly, whereas with the enzyme catalyst the conversion is practically negligible when compared with the exchange reaction. This is a remarkable fact since in the vapour phase reaction it was found that the *para-ortho* conversion was the quicker process. This behaviour immediately indicates that in the two systems two different mechanisms are responsible for the exchange reaction.

TABLE XI.

Pt-black — 80 per cent. D₂O — *p*-H₂.

Minutes.	Per Cent. D.	$\left(\frac{D-D_{\infty}}{D_{\infty}}\right)_{100}$	Per Cent. <i>p</i> -H ₂ in Excess.
0	0	100	100
6.3	4	93	95
15	12	78	89
28	27.5	49	80
38	35	38	52
50	39	30	—
60	50	—	—
(in equilibr.)			

TABLE XII.—*B. coli* — H₂O — *o*-D₂.

Time in Minutes.	Per Cent. D.	Per Cent. <i>o</i> -D ₂ in Excess.
0	100	100
84	88	99
124	77	100
250	64	98
286	62	95

6. Discussion.

The dependence of the conversion on pressure gives information as to the concentration of water and deuterium on the surface. Since the inhibition of the *parahydrogen* conversion by water vapour is completely reversible it is most probably due to the surface of the catalyst being covered by an adsorption layer of water. The amount of water covering the surface is then proportional to the inhibition effect. On the other hand, the concentration of the hydrogen in the adsorption layer will be proportional to the absolute rate of conversion or to the expression "pressure/half-life time" listed in Tables V. and VII., column 4. The adsorption isotherms so obtained are shown in Fig. 4 for temperatures

* The author is very much indebted to Dr. J. Yudkin for the trouble he has taken in preparing the *B. coli* culture.

round 230° C., the concentration in the adsorption layer being given in arbitrary units. It is evident that whereas the curve for H₂O is characteristic for strong adsorption that for hydrogen indicates weak adsorption, the concentration in the adsorption layer being nearly proportional to the pressure. Qualitatively the same conclusion can be drawn from the pressure dependence of the exchange experiments. Again the absolute rate of exchange varies nearly linearly with the deuterium pressure but is not much dependent on the water pressure.

With regard to the energetics of the individual processes involved in the exchange reaction between deuterium and water vapour we may draw conclusions from the activation energies obtained (see Table XIII.). The activation energy for the *para*hydrogen conversion in the absence of water can be attributed to a process involving dissociation of the molecules and probably migration of the atoms.

The difference between the activation energies for the conversion in the presence and absence of water vapour, *i.e.*, 4.4–7.3 K calories, is to be regarded as the heat of adsorption of water on platinum, whereas the apparent energy of activation of the exchange is characteristic for the rate-determining step itself.

TABLE XIII.

	Activation Energy on the	
	Less Active Wire.	More Active Wire.
Exchange reaction	13.5	—
<i>p</i> -Conversion in the presence of water	10.8	13.7
<i>p</i> -Conversion in the absence of water	—	6.4
<i>p</i> -Conversion on the flashed wire	—	5.0

The next question to decide is what is this rate-determining step. It is certainly not the dissociation of hydrogen or deuterium molecules, since it has been found that the *para*conversion proceeds about 10 times, and on the wire in its most active form about 100 times, more quickly than the exchange. That this is not necessarily always so is clearly shown by the exchange experiments involving liquid water.

In the experiments with liquid water on the contrary it was found that the *para-ortho* conversion was the slow process especially with the enzymes of *B. coli* as catalyst, when there was hardly any conversion to be observed at all. Obviously in liquid water the dissociation of the hydrogen molecules is the rate-determining step, and this is immediately followed by the actual exchange reaction proceeding, at such a high speed that the atoms once formed have little or no chance to recombine to normal molecules and thus cause a conversion. This quickness of the exchange reaction becomes understandable if we assume with Horiuti and Polanyi^{1, 2} that in the presence of water not atoms but ions are produced, from the hydrogen molecules. Naturally the exchange of hydrogen ions so produced with the hydrogen or deuterium ions of the water will proceed in general more quickly than the discharge of two ions and the subsequent recombination to normal molecules.

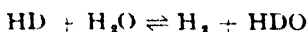
On the other hand, in the catalysis of the gaseous exchange reaction the irreversible poisoning of the activated wire by traces of water vapour

suggests itself as the process connected with the rate-governing step in the exchange reaction. This poisoning effect of water is similar to that of NH_3 found on an iron catalyst.⁴ The irreversibility of the poisoning and its removal by heating the wire in hydrogen or glowing *in vacuo* could be attributed to the formation of some kind of a surface oxide or hydroxide which is reduced by hydrogen or decomposed at high temperatures. If the reduction of this surface oxide proceeds quickly enough an exchange reaction is observed, and it is most probable that actually the reduction of this surface compound is the rate-determining step in the exchange reaction. A direct proof for this view could be given by showing that the dependence of the rate of removal of this surface compound on temperature runs parallel with that for the exchange reaction. Such an investigation is planned also in connection with the catalysis of this exchange reaction by iron and copper in comparison with the reduction of iron and copper oxide.

From the results of the present investigation we may construct the following picture of the interaction of water and hydrogen on the surface of platinum. After having flashed the platinum wire its surface is more or less bare. Hydrogen molecules are readily dissociated into atoms on this surface, and the atoms also readily recombine to molecules. If water molecules come into contact with the platinum they are immediately very strongly taken up and form a stable film of hydroxide or oxide covering most of the platinum surface. This film cannot be pumped off. A further amount of water is adsorbed reversibly, covering the areas left bare by the hydroxide film. In the presence of hydrogen and water with increasing temperature, first the reversibly adsorbed water layer is removed, then the hydroxide film begins to interact with hydrogen and is eventually reduced and removed. The formation and reduction of surface hydroxides takes place alternately and when with sufficient speed the catalysis of the exchange of hydrogen and deuterium atoms between the light or heavy water and hydrogen sets in.

Summary.

The catalytic exchange reaction between deuterium and water vapour



occurring on a platinum wire has been investigated at pressures of 10–70 mm. and in the temperature region 250–410° C. The speed of the exchange reaction has been compared with the *ortho-para* conversion and hydrogen which proceeds about 10 times more quickly.

The pressure dependence of the exchange reaction and conversion reveals that under the experimental conditions water is strongly adsorbed and hydrogen weakly. It has been shown that by glowing the filament *in vacuo* or heating it in hydrogen a very active catalyst is obtained for the *para-ortho* conversion which is, however, irreversibly poisoned by traces of water vapour. This poisoning effect is to be distinguished from a reversible inhibiting effect of the presence of water vapour on the rate of the *para-ortho* conversion.

As apparent energies of activation the following values have been found :

For the exchange reaction	13.5 K cal.
For the conversion reaction in the presence of water	10.8–13.7 K cal.
For the conversion reaction in the absence of water	6.4 K cal.
For the conversion reaction on the activated wire	5.6 K cal.

Most probably the lowest energies of activation are to be connected with the dissociation and migration of hydrogen. It is suggested that the

difference between the energies of activation for the conversion reaction in the presence and absence of water vapour is the heat of adsorption of H_2O on platinum and the apparent energy of activation for the exchange reaction is characteristic for the rate-determining process itself. It is shown that the rate-determining step in the exchange reaction is not the dissociation of the deuterium molecule. This is in contrast to the mechanism of the exchange reaction involving liquid water catalysed by enzymes or platinum black, when the conversion reaction is relatively slow and the rate depending step for the exchange is the ionisation as shown by Horiuti and Polanyi. It is suggested that in catalysis of the gaseous reaction the reduction of a surface oxide or hydroxide formed by the interaction of water vapour and platinum is the rate governing step.

The author has much pleasure in expressing his appreciation of the interest Professor E. K. Rideal, F.R.S., has shown in this work. He is also indebted to the Imperial Chemical Industries, Ltd., for financial assistance.

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THE SWELLING OF PROTEIN FIBRES. PART V. THE SWELLING OF SINGLE COLLAGEN FIBRE BUNDLES UNDER LOAD.

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(From the Laboratories of the British Leather Manufacturers' Research Association.)

The swelling of single collagen fibre bundles teased out of mammalian hides or skins has been described in previous communications (Marriott, 1932¹ and Jordan Lloyd, Marriott and Pleass, 1933).² In this earlier work, changes in length and breadth over a range of p_H from 0 to 14 were followed for fibres both from fresh hide and from hide which had been treated to remove non-collagenous proteins and subsequently dried by extraction with acetone. The fibres were allowed to swell under a light load of about 0.25 g. The fresh and dried fibres show similar behaviour according to the p_H of the surrounding fluid but the degree of swelling was found to be widely different in the two cases, the fresh fibres swelling more freely than the dried. Fresh fibres and dried fibres differ also in another particular—the collagen fibrils of which they are composed are held together by encircling sheaths of reticular tissue (Kaye, 1929)³ which, in fibres strongly swollen in acid or alkali, are ruptured, the remains of the non-elastic reticular sheath becoming visible as constricting bands seen at intervals along the swollen and distorted fibres (Kaye and Jordan Lloyd, 1924).⁴ The behaviour of the reticular

¹ *Biochem. J.*, 1932, **26**, 46.

² *Trans. Faraday Soc.*, 1933, **29**, 554.

³ *J. Internat. Soc. Leather Trades' Chemists*, 1929, **13**, 73.

⁴ *Proc. Roy. Soc., B*, 1924, **96**, 293.

sheath varies with different fibres and under different conditions. It is more readily ruptured in fibres from adult animals than in those from young animals (Jordan Lloyd and Marriott, 1935,⁵ Leplat, 1935),⁶ and it seems to be more readily ruptured in fibres from fresh hides or skins than in those from dried hides or skins. In support of the latter contention it may be mentioned that fibres from commercial air-dried hides or skins do not show constricting rings when swollen in acid or alkaline solutions, though fibres from similar material which has been treated for some days with a suspension of lime containing fair amounts of sodium sulphide in solution will, after deliming and swelling in acid solutions, show some constricting rings. The rings can also be seen in fibres from acetone-dried material when swelling freely though they disappear if the fibres are put under load (Marriott). Since the acetone-dried fibres swell less under the same conditions than the fresh fibres, it seems clear that the reticular sheaths are less easily torn. In the present work, where it was desired to use the same fibre in a number of experiments, this was obviously an advantage. Fresh fibres after two or three loadings and swellings were found to fray out and become disorganised. Hence only fibres from pieces of ox-hide purified and dried with acetone by the method previously described (Jordan Lloyd, Marriott and Pleass) have been used in the present work.

The fibres used in the experiments were fixed at their lower ends and the upper ends were clipped to a thin wire, to the free end of which a variable load could be applied. Changes in length and breadth for changes in load and for changes in p_H of the surrounding fluid were measured photographically by the method previously described (Marriott). The behaviour of the fibres under identical conditions varied to some extent. This is doubtless due to structural causes. The fibres were about 0.1 mm. wide, and showed reversible extension of 1 ± 0.4 per cent. for every gram of load. Generally they broke under loads of 7 to 10 g. though a few fibres could carry a load of 13 grams. One gram load is equivalent to a stress of rather less than 200 lbs. per sq. inch. The breaking stress of the fibres is therefore of the order of 1400 to 2000 lbs. per sq. inch.

Experiments with dry fibres showed that their extension under load was approximately half that of the wet fibres. The extension was reversible on removing the load. The breaking stress was rather higher than for wet fibres.

Experimental.

(A) The Elasticity of the Fibres.

Since it was noticed early in the work that no two fibres behave in exactly the same way under varying conditions it was convenient to use the same fibre for a number of experiments. It was therefore important to establish whether the fibres under load behaved like elastic or like plastic bodies. This was rendered all the more important in view of the fact that Chernov (1936)⁷ has recently shown that leather under repeated small mechanical stresses shows plastic properties. Although it had previously been shown that repeated swelling and de-swelling of a fibre without load in hydrochloric acid induces a permanent change in its properties, fibres can maintain their elastic properties unimpaired for over thirty loadings

⁵ *Proc. Roy. Soc., B*, 1935, 118, 438.

⁶ *Collegium*, 1935, 707, 513.

⁷ *J. Internat. Soc. Leather Trades' Chemists*, 1936, 20, 121.

under varied experimental conditions. This is illustrated by reference to Fig. 1 which shows the behaviour under load of fibre No. 1 when stretched in water. This occurred at the 1st, 5th, 9th, 16th, 21st, 25th, 29th and 33rd loadings (only 4 of these loadings are shown in Fig. 1). Other intermediate loadings took place in hydrochloric, nitric and acetic acids and sodium and potassium hydroxides. Over the whole range of experiment, length in water for a given load remained the same. Continuous experiment has a more marked effect on width. Width in water for a given load becomes somewhat erratic after about 25 loadings. The extensibility of the fibres is therefore independent of internal changes in structure which lead to an increase in diameter. This is shown even more clearly on repeated loadings in lime water. Fibres No. 5 and No. 6 were stretched in water and in a saturated solution of lime water. In the latter, loading

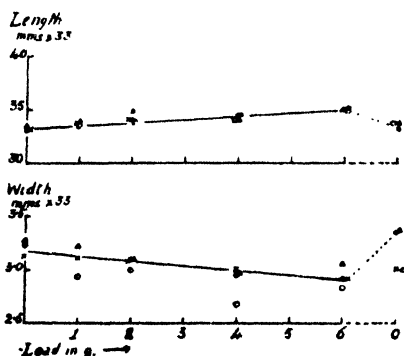


FIG. 1.

● = 1st loading
 Δ = 5th "
 × = 25th "
 O = 33rd "
 } in water. Fibre 1.

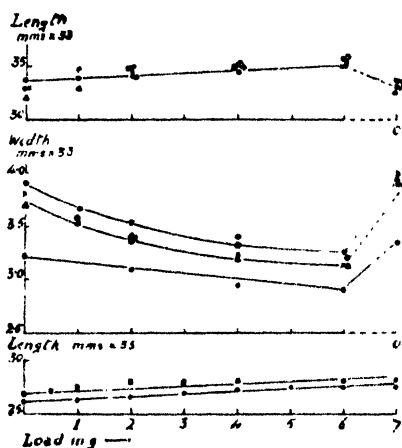


FIG. 2.

● Fibre 1 in Water.
 × " " " N/1000 HCl.
 ○ " " " " HNO₃.
 Δ " " " " H₂SO₄.
 ● Fibre 2 " " Water
 □ " " " 2MNaNO₃ } bottom figure.

took place at once and at one day intervals up to 7 days. For the first 6 days the extensibility of the fibres was unchanged although they were gradually increasing in width throughout the whole time.

In all experiments on loading the fibres, initial and final measurements were taken of fibre dimensions without load. Recovery was very rapid and in most cases complete.

The elastic limits of the fibres were therefore not exceeded within the range of the experiments and the elasticity is evidently founded on some very stable fundamental structure.

(B) Behaviour Under Load at Various pH Values.

When stretched in water, the length of the fibre plotted against the load gives a straight line with most fibres. With a few, stretching is greater in proportion for the light loads. This is due to the dry fibres having become crumpled and part of the gain in length for light loads is due to the straightening of the fibre. The percentage elongation per unit of load varies slightly with the different fibres but is of the order of 1 per cent. per gram (Fibre No. 1). The percentage decrease in width is also uniform and of the order of 0.5 per cent. per gram.

In solutions which do not induce contraction in fibre length (such as $N/1000$ HCl, $N/1000$ HNO₃ and $N/1000$ H₂SO₄, $N/100$ CH₃COOH, $2M$ NaNO₃, $N/10$ HCl + $2M$ NaCl, and, in many cases, $N/20$ Ca(OH)₂), the elongation of the fibre under load is the same as in water. Although the actual width of the fibre may be very different under the different circumstances, the diminution of width under load is similar (Figs. 2, 4 and 5).

In water and in $N/10$ HCl + $2M$ NaCl, (neither of which induces an increase of width) width is a straight line function of load (Fig. 8). In solutions which cause increase of width without contraction in length this simple relation no longer holds, and some loss of water occurs over and above that squeezed out by the stretching of the fibre. This water may have simply diffused freely in between the fibrils, which can always be seen as distinct entities under these conditions. It will be suggested later that the bulk of the water which enters the fibre from these solutions becomes bound to the collagen molecules of the fibrils and is not displaced by a pull along the fibre axis.

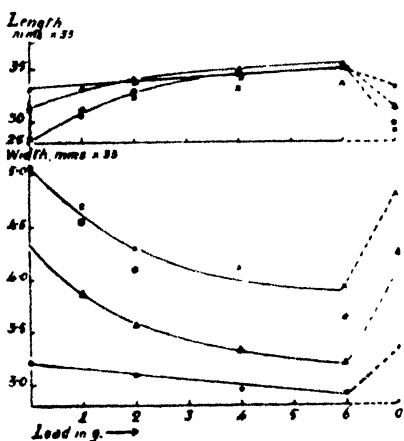


FIG. 3.

- Fibre 1 in Water.
- × " " " $N/100$ HCl.
- ⊙ " " " HNO₃.
- Δ " " " H₂SO₄.

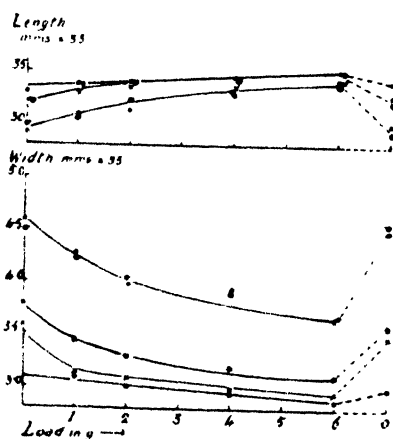


FIG. 4.

- Fibre 1 in Water.
- " " " $N/20$ NaOH.
- ⊙ " " " KOH.
- Δ Fibre 1 in $N/20$ Ca(OH)₂ (after 15 mins.).
- ★ Fibre 1 in $N/20$ Ca(OH)₂ (after 48 hrs.).

With solutions which induce contraction in length, however, this contraction is always associated with an increase of width and volume. The gain in volume is brought about by absorption of water due to osmotic forces. Solutions such as $N/100$ HCl, $N/100$ HNO₃, $N/100$ H₂SO₄, N CH₃COOH, $N/20$ NaOH, $N/20$ KOH all lead to absorption of water under osmotic forces with contraction of length and increase of width. The first effects of loading such water-distended fibres is to squeeze out the osmotic water with a resultant gain in length and loss in width. The fibre elongates rapidly with increasing loads up to about 3 to 4 grams, after which in the case of $N/20$ NaOH, and $N/20$ KOH the curve of length to load runs parallel to that found when stretching in water. In acid solutions the fibre becomes more extensible as the p_H falls. (See Figs. 3 and 4.)

A striking feature of the behaviour of these osmotically distended fibres under load is that while it is comparatively easy to extend the contracted fibre to its original length in water, the width may remain considerably greater than the original width in water. This can be seen with fibres swollen in dilute strong acids and in alkalis (Figs. 3 and 4). It is

particularly striking with acetic acid (Fig. 5). This is also borne out by reference to the p_H -length and p_H -width curves for fibres in hydrochloric

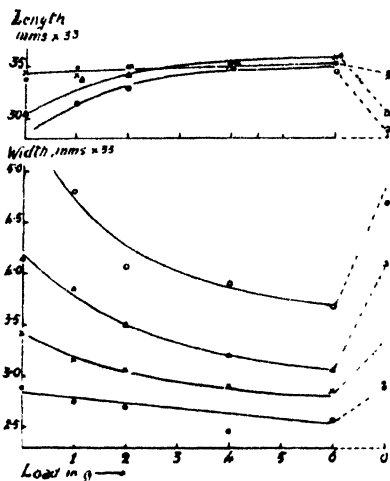


FIG. 5.
 ● Fibre 1 in water.
 × " " " N/100 CH_3COOH .
 Δ " " " N/10 " "
 O " " " N " "

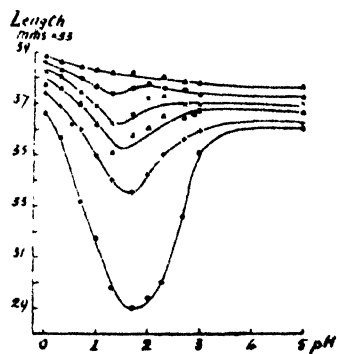


FIG. 6.
 ● Fibre 3 in HCl without load.
 + " " " " with 1g. "
 Δ " " " " " 2g. "
 × " " " " " 3g. "
 O " " " " " 5g. "
 Δ " " " " " 7g. "

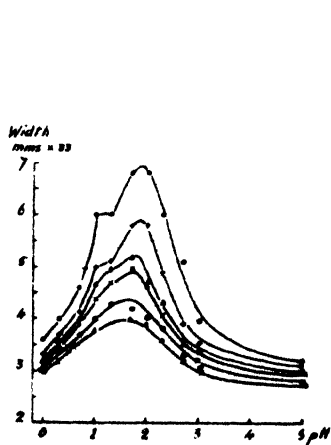


FIG. 7.
 ● Fibre 3 in HCl without load.
 + " " " " with 1g. "
 Δ " " " " " 2g. "
 × " " " " " 3g. "
 O " " " " " 5g. "
 Δ " " " " " 7g. "

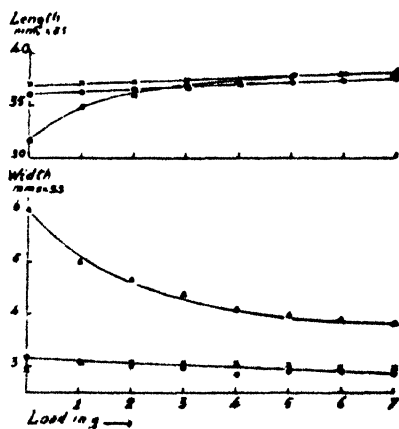


FIG. 8.
 ● Fibre 4 in Water.
 Δ " " " N/10 HCl.
 × " " " N/10 HCl + 2MNaCl.

acid. A load of 7 grams is sufficient to extend the acid-swollen fibre back to normal length (Fig. 6) but is insufficient to bring it back to normal width (Fig. 7).

Discussion.

The absorption of water by a collagenous tissue such as a hide or skin has long been recognised in the tanning industry to occur in two different manners. Hides or skins may become distended with water or "plumped" in which case they are turgid and translucent. This occurs in acid or alkaline solutions in the absence of dissolved salts. They may however become swollen with water yet remain flaccid and opaque. This occurs in salt solutions. Microscopical examination shows that the fibres in the former case are glassy and closely packed and pressed together; in the latter the weaving is much looser and the individual fibrils of the fibres can be clearly seen. Marriott has previously pointed out that in the isolated fibre bundles these two types of water absorption can be distinguished. In the present work the distinction is even more clearly marked. "Plumping," which occurs in acid and alkaline solutions and is characterised by a shortening of the fibre, can be reversed by loading the fibre. Swelling which occurs in salt solutions and also is now shown to accompany "plumping" is characterised by an increase in width of the fibre and cannot be reversed by loading the fibre—it can, however, be reversed by washing the fibre thoroughly in water.

It is now possible to differentiate the chemical bases of these two types of water absorption. "Plumping," (which is characteristic of acid solutions, shows a maximum at about p_H 1.7 for acetone-dried fibres and is completely suppressed by the presence of dissolved salts—see Fig. 8), is due to salt formation between the collagen and the acid and the establishment of a Donnan equilibrium. The fibres absorb water and swell, the monovalent strong acids causing more swelling than the divalent (see Fig. 3). Owing to the lateral bindings of the collagen molecules which lie parallel to the fibre axis, the water drawn in under the osmotic forces of the Donnan equilibrium can only be accommodated at the expense of the fibre length, *i.e.*, the water forces the molecules to bulge sideways in the regions between the collateral bindings (Jordan Lloyd, 1932).⁶ By pulling out the fibre, the osmotically-held water is forced out. The force required to expel this water is about 7 gram load on a fibre of 1 mm. diameter or approximately 1500 lbs. per sq. inch. The osmotically held water can be regarded as "free," as far as the protein is concerned and the order of the forces required to expel it from the system is less than the order of the forces required to expel the loosely bound water of iso-electric gelatin in equilibrium with water. Jordan Lloyd and Moran (1934)⁷ find that 8000 lbs. per sq. inch is required to remove the latter. Osmotically held water leads to a loss in fibre length and gain in fibre width. Loading the fibre restores the length and very largely restores the width.

When acids act on collagen fibres they do not merely produce a Donnan equilibrium, but have two other effects, *viz.* (a) to cause the loaded fibres to lengthen slightly and to develop a slightly greater extensibility (see Fig. 6), and (b) to increase the width over and above that due to osmotic swelling (see Fig. 7). They also weaken the reticular tissue at p_H values of 1.2 or less, leading to additional swelling (Jordan Lloyd and Kaye and Jordan Lloyd, Pleass and Marriott, also Fig. 7). If the elasticity of the fibres is to be interpreted on Astbury's theory that the

⁶ *J.S.C.I.*, 1932, **51**, 141.
⁷ *Koll. Z.*, 1926, **40**, 264.

⁸ *Proc. Roy. Soc., A*, 1934, **147**, 382.
⁹ *Biochem. J.*, 1927, **23**, 358.

molecules are to some extent coiled but can be pulled out under load, the action of acids is consistent with the theory that they form salts with the collagen molecules, which ionise to form a diffusible and non-diffusible ion and that, in doing so, they break the salt linkages previously acting as lateral bonds between carboxyl groups of one collagen molecule and an amino group of an adjacent one.

Acids, however, have an additional action strictly similar to that of salts, which may be attributed to a "Hofmeister effect"; this shows itself microscopically as a splitting of the fibre into fine fibrils and, as regards dimensions, as a gain in width without alteration in length. The water absorbed under the "Hofmeister effect" of acids and salts is undoubtedly to be regarded as "bound" water. Acetic acid is strongly differentiated from the strong acids in this respect (Fig. 5). As regards osmotic action, it conforms to the same p_H standards but, as regards splitting and gain in width, it is in a class by itself.

Probably the well-recognised fact that all acids have an individual as well as general action on fibres, is due to their "Hofmeister effect" as distinguished from their "Donnan effect."

The action of acids as regards both osmotic swelling (Donnan effect) and as regards lyophylic swelling (Hofmeister effect) is without any permanent effect on the elastic properties of the fibre.

The action of alkalies, like that of acids, can be divided into a "Donnan effect" and a "Hofmeister effect."

The "Donnan effect" or plumping shows very definitely in the case of the monacid bases, sodium hydroxide and potassium hydroxide. With both of these there is diminution in length with gain in width. In the case of calcium hydroxide the "Donnan effect" is not always evident, some fibres showing a slight shortening and others apparently, showing none. There is a latent period from p_H 5 (the iso-electric point of collagen) to p_H 11.2 over which there is no "Donnan effect" showing itself as a shortening of the fibre. A splitting or "Hofmeister effect" showing itself as a gain in width starts about p_H 9. This splitting action of the fibre into its constituent fibrils is evident on microscopical examination and is a very conspicuous feature of the action of lime water. As regards the action of alkalies on the reticular sheaths, evidence is somewhat lacking. Kaye¹⁰ has reported that they are not affected by lime but are weakened by sodium sulphide. The absence of any well-defined peak of alkaline swelling for collagen fibres suggests that the reticular tissue is weakened in sodium hydroxide solutions of $N/10$ strength or thereabouts.

Alkalies of moderate concentration seem to be without effect on the elastic properties of fibres and there is no tendency for the loaded fibres to gain in length in alkaline solutions or to become more extensible.

The action of salts on fibre swelling appears to be purely a "Hofmeister effect." There is much microscopical evidence that salts cause splitting of the fibres into their constituent fibrils with a gain in width. Nitrates show this very clearly. Salts do not cause any noticeable change in fibre length but there appears to be a slight elongation in some cases. Salts ($2M$ $NaNO_3$, Fig. 2) have no effect on the elastic properties of the fibres.

¹⁰ *J. Internat. Soc. Leather Trades' Chemists*, 1936, **20**, 223.

Summary.

1. Collagen fibres have, over a wide range of conditions, elastic properties which appear to be those of the fundamental molecular structure of the fibrils. Wet fibres have about twice the extensibility of dry fibres, namely about 7 per cent. extension at the elastic limit.

2. Collagen fibres can absorb water and swell under two independent sets of forces, those due to (1) the formation of a Donnan equilibrium which is controlled by the p_H of the system and (2) a Hofmeister effect of dissolved acids, bases or salts, in which each chemical reagent produces its own characteristic effect.

3. It is suggested that the Donnan or p_H effect is osmotic and leads to an increase of free water in the system while the Hofmeister effect leads to an increase of bound water.

4. The water absorbed under the action of acids or alkalies (Donnan effect) leads to a shortening of the fibre but can readily be removed by loading the fibre. The shortening is accompanied by increase of width which is reversed on loading the fibre.

5. The water absorbed under the action of salts or very dilute acids or alkalies leads to an increase of width without shortening (Hofmeister effect). This increase is not reversed on loading the fibre. Acids and alkalies at concentrations which cause shortening also show this non-reversible gain of width.

6. The order of the forces required to remove the osmotic water from acid swollen fibres is less than that required to remove the loosely bound water from iso-electric water-swollen gelatin.

7. Strong swelling in acid solutions ($p_H < 1$) leads to a tearing of the reticular sheaths round the fibres with a consequent further absorption of water, but apparently with no change in the elastic properties.

THE ROENTGENOGRAPHIC STUDY OF ZINC AND CADMIUM FILMS DEPOSITED IN THE PRESENCE OF COLLOIDS.

(A PRELIMINARY COMMUNICATION).

BY L. PALATNIK.

Received 20th January, 1936.

As is well known, colloids are introduced into the electrolytic bath for the purpose of obtaining bright, finely-grained depositions. We studied by X-rays Zn films deposited in the presence of dextrine, and Cd films deposited in the presence of dextrine, sulphonated castor oil and cereal extracts. The conditions of deposition are given in Table I.

It follows from the work of Glocker and Kaupp,¹ and other workers, that during the electrolytic deposition of Cu, Ag, Cr, Ni and Fe in baths of corresponding compositions (in the absence of colloids) there are formed textures, the degree of perfection and axis of which depend on the conditions of the deposition (current density, electrolyte composition, etc.).

Bozorth's researches² have shown that no texture is observed for

¹ Glocker a. Kaupp, *Z. Physik*, 1924, **24**, 121.

² Bozorth, *Physical Rev.*, 1925, **26**, 390.

Zn and Cd. It is seen, however, from the X-ray diagrams (Figs. 1-2) that, during the electrolytic deposition of these metals (Zn and Cd) in the presence of above-mentioned colloids, a texture can be observed, although an imperfect one, particularly for Zn. (See diagrams facing p. 869.)

For Zn, the (221) planes tend to lie parallel to the surface. We discovered also that the degree of the orientation of crystals depends on the concentration of colloids in the electrolyte (Figs. 3, 4, 6), as well as on the current density (Figs. 4, 5). We propose to make use of this fact as a method for determining the "effective concentration" of a colloid in the bath. The relative intensity of the Debye-gram lines for Zn and Cd films undergoes a sharp change depending on the concentration of the freshly-prepared colloid (Figs. 3, 4, 6, 8, 9, and 10).

TABLE I.

Composition of Electrolyte.	Current Density	Time of Exposure	Cathode.
1. Deposition of Zinc.			
ZnSO ₄ 240 gm	2 and 5 amp / dcm ²	10, 20 and 40 minutes	Fe
AlCl ₃ 15 "			
Al ₂ (SO ₄) ₃ 30 "			
H ₂ SO ₄ 0.5 "			
H ₂ O 1 litre			
Dextrine : 0, $\frac{1}{2}$, $\frac{1}{2}$, 1, 2, 4, 6, 8 and 10 gm			
2. Deposition of Cadmium.			
CdO 16 gm.	0.75, 1 amp / dcm ²	10, 30 minutes	Cu and Fe
KCN 200 "			
H ₂ O 1 litre			
The colloids			
Cereals extracts 0.25, 0.5, 1 gm			
Sulf castor oil 0.1, 0.2, 0.5, 1 "			
Dextrine 0.5, 1 "			

As has already been observed during the operation of a bath, there occurs in the course of time a gradual "disappearance" of the colloid. For this reason it seems to be advisable under factory conditions to verify the "effective concentration" of a colloid. The author has obtained a series of X-ray diagrams for Zn and Cd deposited from various concentrations of freshly-prepared colloids (but under the same other conditions of current density, time of electrodeposition, composition of electrolyte, material and treatment of the cathode, etc.), which serve as standards for every control determination of the "effective concentration" of the colloid in the given electrolyte. Thus, the analysis can be accomplished within from 3 to 5 hours.

The Debye-grams were taken with a plane sample, at an angle of 47° to the original beam (a different angle may be used so long as the same angle is always maintained for the determinations) of the Fe or Cr radiation (the anti-cathode may also vary).

We also noticed an increase in the brightness of films, with the degree of orientation of crystallites. This very phenomenon has recently been observed by Wood² for Cr and Ni electrodeposited in corresponding baths (not containing colloids).

² Wood, *Trans. Faraday Soc.*, 1935, 31, 1248.

Thus we can now take it for certain that, in the case of Cd and Zn, colloids bring about the formation of a texture, *i.e.*, they promote the growth of crystals in a single crystallographic direction, *viz.*, perpendicular to the surface of the cathode (see also ⁴).

*Electro-Mechanical Works,
Kharkov, U.S.S.R.*

⁴ Froelich, Clark, Aborn, *Trans. Electrochem. Soc.*, 1926, 49, 369.

THE COLOUR AND OPACITY OF EMULSIONS.

BY JAMES FREDERICK MORSE.

Received 30th March, 1936.

The mixing of an aqueous liquid with an oily liquid usually results in a creamy emulsion, due to the differing refractive indices and optical dispersive powers of the two phases. When the two liquids have the same value for refractive index and optical dispersive power a transparent emulsion is obtained. Holmes and Cameron ¹ have shown that if emulsions be made of two liquids of equal refractive indices (ensuring transparency) but widely different optical dispersive powers, the system is comparable to a multitude of lenses or prisms with consequent prismatic colour effects. The optical properties of these chromatic emulsions have been described by Sogani.²

Some experiments ³ have been carried out on dilute castor oil emulsions with polarised light, and Teorell ⁴ using dilute ultramicroscopic emulsions of mastic investigated their optical properties together with those of sols of gelatin and ferric hydroxide.

Bechhold and Hebler ⁵ in their nephelometric investigation of graded suspensions of barium sulphate found that the light scattered increased as the particle size decreased from $2.5\ \mu$ to $800\ \mu\mu$, but thereafter decreased.

No work appears to have been reported concerning the opacity of emulsions as influenced by the concentration and degree of dispersion of the internal phase and the subsequent effect on the final colour of the emulsion should one of the phases be coloured.

Several systems of colour measurement are in vogue for dealing with transparent and opaque material. Semi-opaque and translucent systems present difficulties, since the former are insufficiently opaque to be gauged by reflected light and the latter scatter too much light to permit measurement by the transmission method. Visual and photo-electric methods of colour recording are available. Of the former that of Lovibond is the best known, but for more scientific data a form of spectrophotometer is usually employed.

¹ *J. Am. Chem. Soc.*, 1922, 44, 71.

² *Phil. Mag.*, 1926, 1, 321; *Proc. Ind. Assocn. Cult. Sci.*, 1920-21, 6, 134.

³ D. S. Subbaramaiya, *Proc. Ind. Acad. Sci.*, 1935, 1A, 709; R. S. Krishnan, *ibid.*, 1935, 1A, 717.

⁴ *Kolloid. Z.*, 1930, 53, 322; 1931, 54, 58; 1931, 54, 150.

⁵ *Ibid.*, 1922, 31, 70.

The apparatus of Toussaint⁶ was the pioneer of commercial photo-electric colorimeters. Designed primarily for the textile trade the colour of opaque and transparent material may be measured. Bolton and Williams⁷ utilising this method for oils introduced an aqueous copper sulphate filter with the object of removing infra-red rays to which photo-electric cells, in general, are very sensitive.

The principle underlying these methods is to direct a beam of light of known wave-length on (in the case of opaque material), or through (in the case of transparent liquids) the sample to be examined. The reflection or transmission is then recorded by a galvanometer connected to the photo-electric cell on which the light falls after leaving the sample. Immediately after or before the above reading is taken, the light is di-

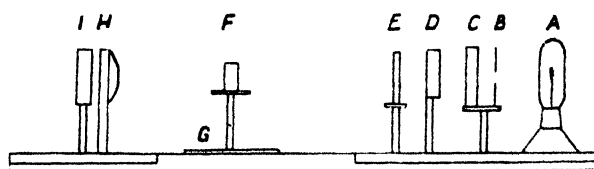


FIG. 1 (A).

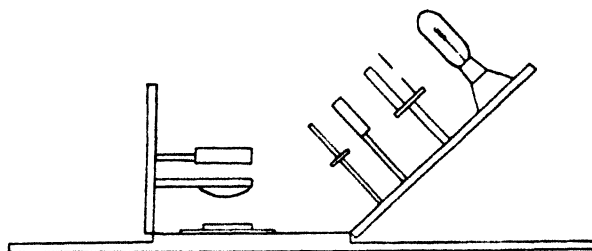


FIG. 1 (B).

rected upon a standard and from this reading the percentage reflection, or transmission of the sample is calculated. In the case of opaque material the standard may be a block of pure calcium sulphate or magnesium carbonate, while water or colourless oil, as occasion demands, serves as a standard for trans-

parent liquids. Six readings are usually taken, using filters approximately to traverse the visual spectrum.

The following Wratten filters were employed in the apparatus to be described :—

49 (C4), 75, 62, 73, 72, 70.

A spectrographic examination of the filters revealed that the predominant wave-lengths transmitted were :—

4200Å, 4600Å, 5000Å, 5400Å, 5700Å, 6400Å respectively.

The apparatus constructed in these laboratories is shown diagrammatically in Fig. 1, arranged for colour measurement of transparent liquids (A), and as employed for opaque samples (B).

The light from the projection lamp A passes through the iris diaphragm B and the copper sulphate filter C contained in a Soyka flask. The light is then directed by the condenser D through the filters E to the standard and samples F which the slide G allows to be rapidly brought into the beam of light. The condenser H collects the light when it is directed upon the Weston photonic photo-electric cell I. The current so generated is measured directly to 0.05 micro-ampere and by estimation to 0.01 micro-ampere by a Cambridge Metre. Liquids are contained in 1-inch Lovibond

⁶ See L. Blin Desbleds "Exact Colour Matching and Specifying" (Paris).

⁷ *Analyst*, 1935, 60, 447.

cells and opaque material in ebonite cells 1 cm. deep. The condenser H is not necessary for measurements with transmitted light but its inclusion enables the instrument to be used immediately for opaque or transparent samples.

From the readings obtained the percentage (based on the standard 100 per cent.) transmission or reflection is calculated for the predominating wave-length of light transmitted by each of the six filters. Fig. 2 records the colour curves of 0.1 per cent. Oil Orange and 0.1 per cent. Sudan III. in liquid paraffin, a 1-inch Lovibond cell being used and liquid paraffin as standard. An average of the six percentage transmissions gives the "mean tone" which may be regarded as a measure of brightness irrespective of the actual hue. If such a coloured oil formed the dispersed phase of an emulsion the colour of the emulsion would depend upon the concentration of the oil and the degree of dispersion; the colouring matter determines the hue and the opacity of the emulsion determines the tone.

Fig. 3 shows the effect of dispersion on the tone of a coloured emulsion.

It will be seen that the tone has increased with the degree of dispersion and consequently the opacity. To compare actual increases in the "brightness" of colours it is convenient to calculate the mean tone (as a percentage of the white standard) and plot this against the average globule size. Fig. 4 shows the relation.

It is obvious that irrespective of (a) the particular colour employed, (b) in which phase it is present, and (c) the type of emulsion, (O/W, W/O), the final colour effect will depend on the opacity of the emulsion. This in turn will depend on the refractive indices and optical dispersive powers of

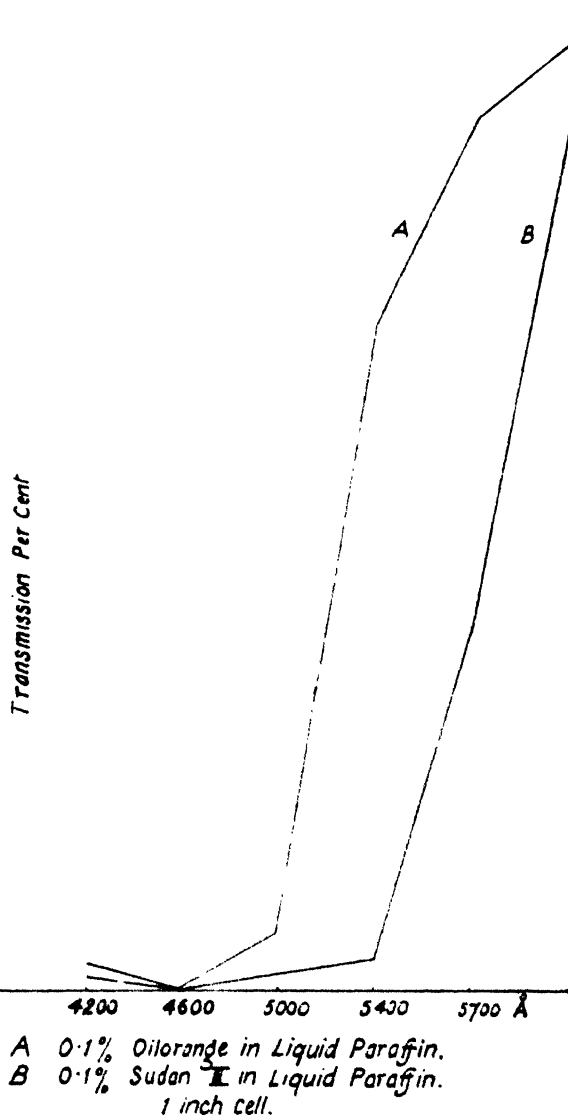
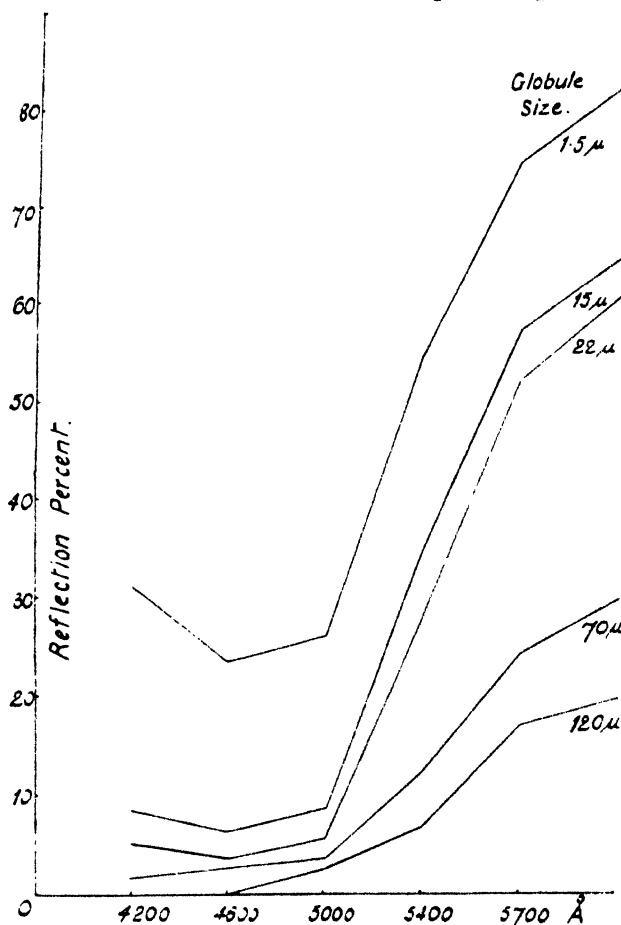


FIG. 2.

the two phases and on the concentration and globule size of the internal phase.

With the refractive indices and optical dispersive powers maintained



10% Liquid Paraffin in Water.
Oil containing 0.1% Sudan III.

FIG. 3.

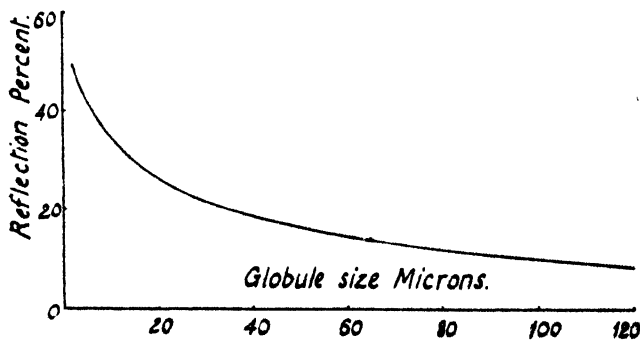


FIG. 4.

constant, the effect of the concentration and the globule size of the dispersed phase was now examined. Emulsions of liquid paraffin were employed as a colourless oil is necessary. The emulsions were prepared by mixing predetermined proportions of fairly low viscosity paraffin ("slab oil") with an aqueous gum solution containing 1.5 grams gum tragacanth and 8.5 grams gum acacia per 100 c.c. Varying degrees of dispersion were obtained as follows:—

(1) Handshaking: 40 c.c. emulsion were shaken 50 times in a 120 c.c. bottle. After determining the globule size and opacity the same emulsion was—

(2) Shaken 50 times in the same bottle, but with the addition of 25 glass beads, 7.5 mm. diameter. After examination the same emulsion was passed through—

(3) "Empire" cream machine whereby the emulsion is forced through a fine orifice partially blocked by a wire. To obtain

a range of dispersions the emulsion was treated up to 10 times in this machine.

(4) The excellently constructed "Impulsor" laboratory homogeniser permitted emulsions of high dispersion. Photomicrographs employing a modified Hvidberg^{*} technique—showed remarkably uniform and highly dispersed emulsions obtained with this machine in which 20 c.c. of mixture were sufficient.

The globule size was determined by means of an eyepiece micrometer, standardised against a 1/100 mm. ruling, and direct examination with a Leitz No. 3 objective for the coarser emulsions and a No. 7 objective for the homogenised emulsions.

Emulsions were prepared of 5, 10, 15, 20 and 50 per cent. concentrations of liquid paraffin in gum solution, varying dispersions being obtained by the methods described above. After recording the globule size the opacity, as measured by the reflection (calculated to a percentage of the white standard - calcium sulphate), of the emulsion was determined in a 1 cm. deep black cell. Fig. 5 gives the "colour" curves of 10 per cent. emulsions of varying grain sizes. The average of the six values gives the mean tone and in Fig. 6, these mean tones are plotted as percentage "opacities" against globule size for a range of oil concentrations. During

the recording of a large number of these "opacities," it was found that the "mean tone" closely corresponded to the percentage reflection using the yellow filter, wave-length 5400Å, and in subsequent work this figure was taken as the opacity.

It will be seen from Fig. 6 that a layer of emulsion 1 cm. deep will appear equally opaque and white irrespective of the fact that the dispersed phase

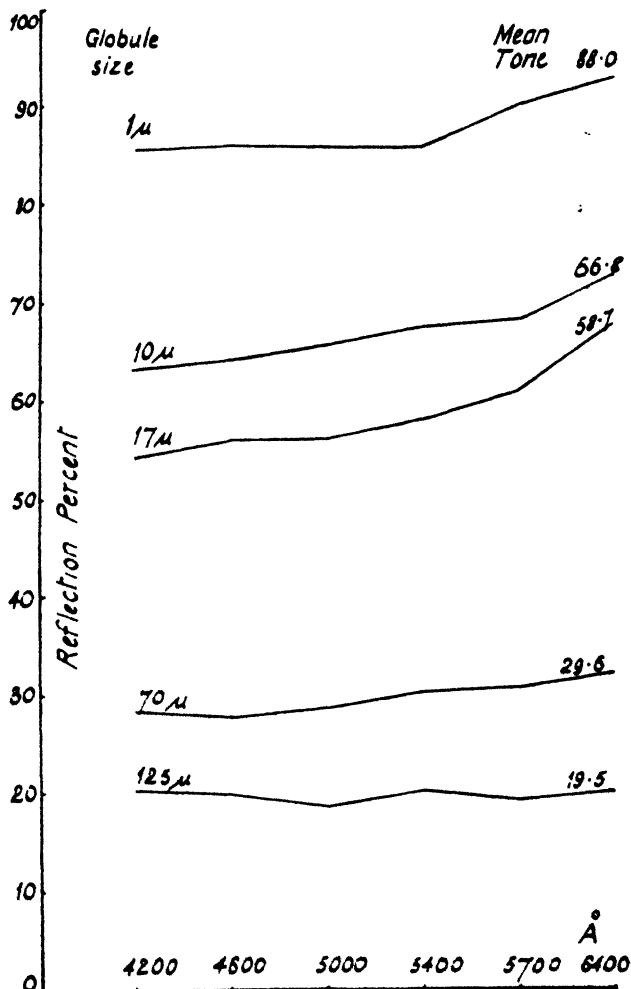


FIG. 5.

* *Kolloid. Z.*, 1935, 72, 274.

may be 5 per cent. or 50 per cent., provided that the globule size is in the neighbourhood of $1\ \mu$.

Maintaining a uniform globule size the effect of concentration was investigated. Emulsions of 25 per cent. liquid paraffin were prepared.

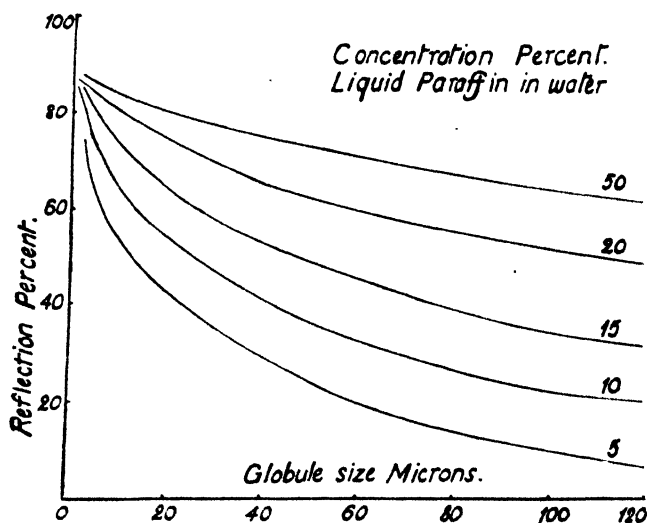


FIG. 6.

and the final homogenisation. When a 25 per cent. emulsion of sufficiently uniform globule size had been obtained, it was diluted to give

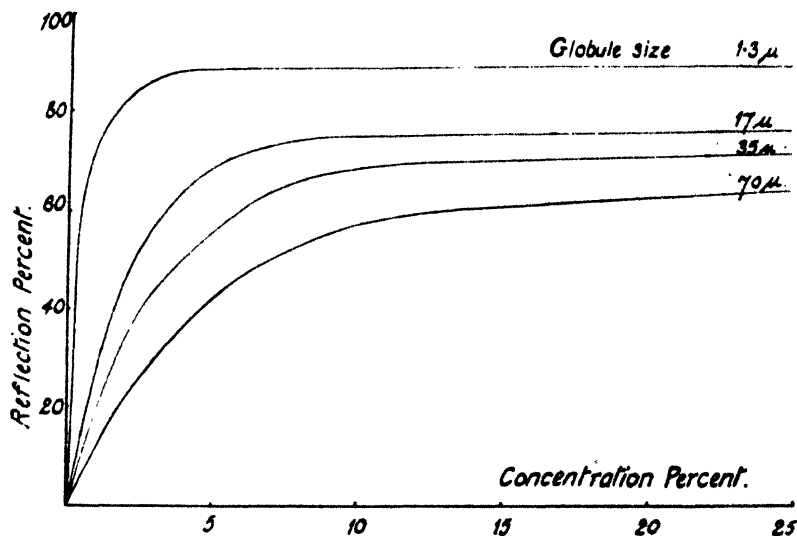


FIG. 7.

a series of concentrations, the opacity of each one being recorded. Fig. 7 shows such a series at various globule sizes. Some discrepancy in opacity at the larger globule sizes is evident between this series and those in Fig. 6, no doubt due to the less uniform emulsions of the latter. At dilute concentrations the effect of globule size is most marked and any irregularities have a pronounced effect.

Figs. 6 and 7 give a guide to the relative opacities to be expected with emulsions in which the phases have optical properties corresponding to those of liquid paraffin and aqueous gum solution. If a coloured solute be present in one of the phases of the emulsion, the resulting colour of the emulsion is a function of the opacity.

Summary.

(1) An investigation has been made relating to the opacity of emulsions as influenced by the factors of concentration and grain-size of the internal phase.

(2) A photo-electric photo-colorimeter and six spectrum filters were employed to determine (a) the effect of grain-size on the tone of a coloured emulsion, (b) the opacity of emulsions of varying grain-size and volume-ratio.

(3) Emulsions of very fine grain, about 1μ diameter, contained in a 1 cm. deep cell, exhibit equal opacities when the concentration ranges from 5 per cent. and upwards. Added oil-soluble or water-soluble colouring matter does not affect this result.

Grateful acknowledgment is made to Dr. William Clayton for his deep interest throughout this investigation, and to Colonel E. A. Rose of the Improved Emulsification Process Company Limited for the loan of the "Impulsor" laboratory homogeniser without which the production of small quantities of the fine grain emulsions would not have been possible.

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IONIC EXCHANGE AND SORPTION OF GASES BY CHABASITE.

BY E. RABINOWITCH and W. C. WOOD.

Received 20th February, 1936.

Chabasite crystals have a skeleton lattice formed by the ions Si^{4+} , Al^{3+} and O^{2-} . The hollows are occupied by positive ions, chiefly Ca^{2+} , and by neutral molecules, usually H_2O . Calcium can be exchanged for other divalent or monovalent ions, water for other molecules of appropriate size.

In a previous paper¹ several dehydrated chabasite samples from different localities, were found to possess about the same power of sorption; one, however—that from Richmond (Victoria)—sorbed three or four times less gas than all the others. Data available in Dörlter's *Handbuch der Mineralogie* indicate that this chabasite is abundant in alkali ions, and we thought that this might be the reason of its low sorptive power. We therefore investigated the sorption by a number of chabasites in which calcium was exchanged for a series of different ions.

¹ E. Rabinowitch, *Z. physik. Chemie*, 1932 (B), 16, 43, further quoted as "Dörlter I."

Experimental.

1. Preparation of the Samples.—The purest crystals of chabasite from Rübesdorfel (Czechoslovakia) were washed in CCl_4 and ground. Portions of 3 gm. were mixed with 30 c.c. of 10 per cent. chloride solutions, and kept at about 100°C . for 200 hours, during which the solutions were replaced three times. The samples were then left exposed to the air for several days to allow them to acquire their "natural" water content, and analysed.

2. Analyses of the Samples.—We investigated samples treated with NaCl , KCl , MgCl_2 , CdCl_2 , CaCl_2 , SrCl_2 , BaCl_2 , and LaCl_3 . Approximately 0.5 g. were dissolved in 400 c.c. of conc. HCl for the separation of SiO_2 . The treatment of the deposits with H_2SO_4 and HF (for the separation of SiO_2 from traces of barium, calcium, etc.), was omitted; the SiO_2 values given in the following tables may therefore be a little too high.

A complete ionic exchange took place with NaCl , KCl and BaCl_2 , and a partial one with SrCl_2 and CdCl_2 . The MgCl_2 sample contained only 2-3 per cent. MgO ; that treated with LaCl_3 was practically identical

TABLE I.—COMPOSITION OF DIFFERENT SUBSTITUTED CHABASITES.

	Original Mineral.	Chabasite treated with the Chloride of				
		Sr.	Ba.	Cd.	Na.	K.
SiO_2	47.5	45.6	42.95	46.7	48.95	48.25
Al_2O_3	19.2	19.2	10.9	18.6	19.2	18.5
CaO	9.15	7.25	1.6	5.55	0.95	0.25
SrO	—	7.15	—	—	—	—
BaO	—	—	18.55	—	—	—
CdO	—	—	—	8.35	—	—
Na_2O	1.1	0.5	0.6	0.8	9.35	1.0
K_2O	1.55	0.9	0.75	0.75	1.25	13.8
H_2O	21.7	19.7	18.9	19.7	20.55	17.8
	100.2	100.3	100.25	100.45	100.25	99.6

TABLE II.—EQUIVALENT COMPOSITION OF THE CHABASITES.

	Original Mineral.	Chabasite treated with the Chloride of				
		Sr.	Ba.	Cd.	Na.	K.
SiO_2	4.2	4.05	4.3	4.25	4.35	4.4
Al_2O_3	1	1	1	1	1	1
CaO	0.85	0.65	0.15	0.5	0.1	0
SrO	—	0.35	—	—	—	—
BaO	—	—	0.75	—	—	—
CdO	—	—	—	0.35	—	—
Na_2O	0.1	0.05	0.05	0.10	0.8	0.1
K_2O	0.1	0.05	0.05	0.05	0.1	0.8
Total valency of the cations	8.1	8.2	7.9	8.0	8.0	7.8
H_2O	6.4	5.8	6.3	5.9	6.05	5.4

with the original material (a spectroscopic test revealed the presence of about 1 per cent. of lanthanum). The sample treated with CaCl_2 was also unchanged; the small quantities of Na_2O and K_2O present in the original mineral were not exchanged for CaO . These three preparations were discarded for the sorption experiments. The composition of the other five, together with that of the original material (which is a typical Ca chabasite), is given in Tables I. and II. Table II. shows that the molecular composition of the samples can be represented by the formula:—



X standing for one mol. of bivalent or two mols. of monovalent ions. The ionic exchange takes place in a strictly stoichiometric way.

The water content of all the substituted chabasites is about the same, that of the potassium chabasite being, however, somewhat lower.²

3. Sorption Experiments.—For each experiment 1 g. chabasite powder was placed in the hard glass tube F (Fig. 1), covered with asbestos

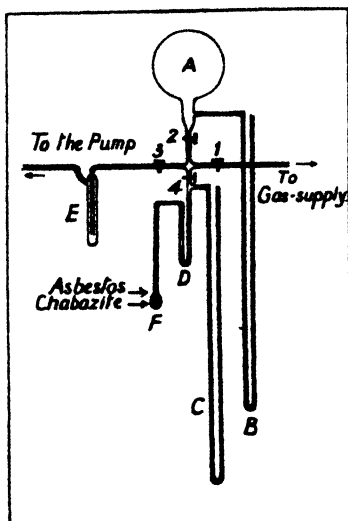
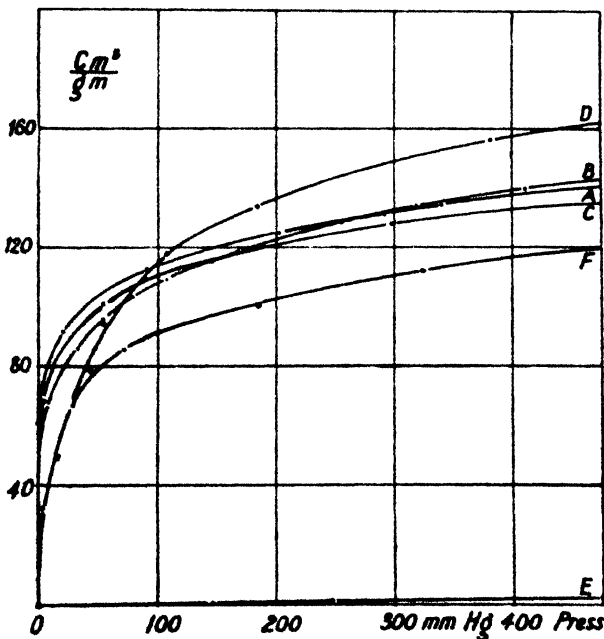


FIG. 1.

FIG. 2.— H_2 Sorption at -190°C .

A	Sr-Chabasite.	D	Na-Chabasite.
B	Cu- "	E	K- "
C	Ba- "	F	Cd- "

wool to prevent sputtering and then heated to 500° for 2 hours, under constant pumping by a mercury pump. Traps D and E were immersed in liquid air (in experiments with CO_2 and C_2H_6 in solid carbon dioxide) to protect the chabasite from mercury and grease vapours. Gases were introduced in small portions from the container A, into the tube F, the quantity introduced being determined by the drop of pressure in A (manometer B), the resulting pressure in F by the manometer C. The quantity of

² E. Gruner (*Z. anorgan. Chemie* (1933), 211, 385) assumes $7\text{H}_2\text{O}$ in the calcium chabasite and $5\text{H}_2\text{O}$ in the alkaline chabasites.

gas sorbed was calculated by subtracting from the total quantity admitted into F the small quantity filling the tubing FD. The same sample was used for experiments with all gases, as it was shown that repeated heating had no effect on its sorbing capacity.

Experimental Results.

A set of successive pressure measurements with increasing gas quantities served to determine a sorption isothermal. In accordance with

Sorption of:	R (c.c./gm.).	R and W (c.c./gm.).
(1) N ₂ (at - 190° C., <i>p</i> = 400 mm.) .	170	163
(2) H ₂ (same conditions) .	130	130
(3) CO ₂ , (<i>p</i> = 100 mm., <i>t</i> = + 20° C.)	110	115

previous experience, the isothermals obtained with H₂ and N₂ were well reproducible; it was, however, difficult to reproduce measurements with CO₂ to more than 10 per cent.

and in the case of C₃H₈ deviations of 50 per cent. were quite possible. This is due to the great velocity with which the equilibrium is reached in the case of H₂ and N₂, the pressure becoming constant a few seconds after the introduction of the gas. With CO₂ one has to wait for an hour or more (at the higher pressures), and a day or more is necessary with C₃H₈. The results obtained with C₃H₈ (Fig. 5), are therefore not very reliable. The sorption values obtained with the natural calcium chabasite were practically identical with those found in Paper I.

The changes in the sorption power caused by ionic exchange are reversible. By treating a sample of potassium chabasite with a solution of CaCl₂, we recovered a calcium chabasite which sorption isothermals were practically identical with those of the original mineral. The results of the sorption measurements are given in Figs. 2, 3, 4 and 5.³

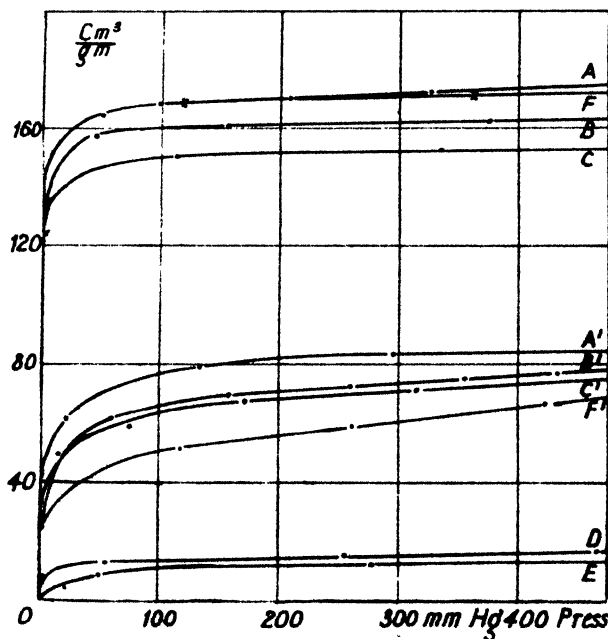


FIG. 3.—N₂ Sorption.

A	Sr-Chabasite	} - 190° C.	A'	} - 80° C.
B	Ca-Chabasite		B'	
C	Ba- "		C'	
D	Na- "		D'	
E	K- "		E'	
F	Cd- "		F'	

³ The numerical data underlying Figs. 2-5 can be found in the dissertation by W. C. Wood, University of Göttingen, 1934.

The conclusions which can be drawn from these isothermals are as follows:—

(a) The three *alkaline earth chabasites* have practically identical sorption properties (the differences observed in experiments with C_3H_8 are not certain enough for discussion).

(b) *Cadmium chabasite* isothermals run somewhat below those of the alkaline earth products, indicating a lower sorption energy. It is, however, probable that the saturation values are the same. The unchanged water content supports this assumption.

(c) *Sodium chabasite* is characterised by a very small sorption capacity for *nitrogen*.

H_2 , CO_2 and H_2O are, however, strongly sorbed. The corresponding isothermals rise at first slower than those of the other chabasites, indicating a smaller initial sorption energy, but attain ultimately even somewhat

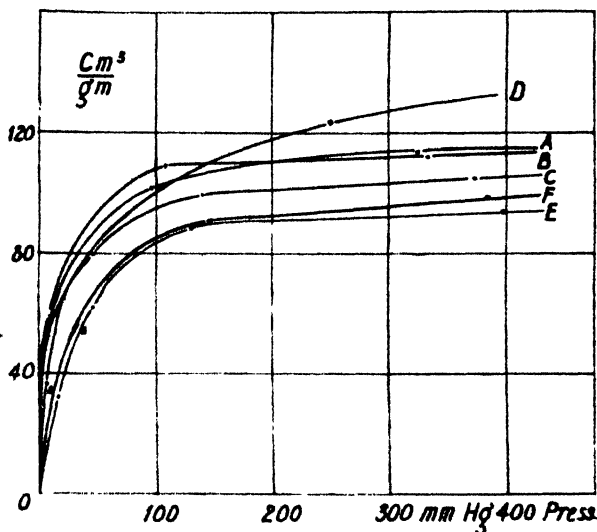


FIG. 4.— CO_2 Sorption at $20^\circ C$.

A Sr-Chabasite.	D Na-Chabasite.
B Ca- "	E K- "
C Ba- "	F Cd- "

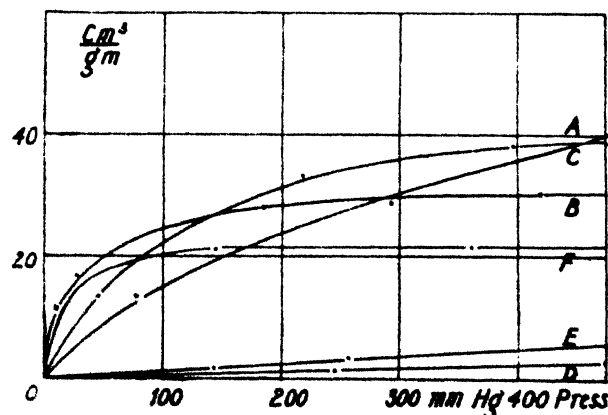


FIG. 5.— C_3H_8 Sorption at $20^\circ C$.

A Sr-Chabasite.	D Na-Chabasite.
B Ca- "	E K- "
C Ba- "	F Cd- "

chabasites. C_3H_8 is only very weakly sorbed both by the sodium and by the potassium chabasite.

higher values. The water content is, however, the same, indicating that the saturation values (and thus the sorption space), may be unchanged in this chabasite too.

(d) *Potassium chabasite* sorbs as little nitrogen as the sodium product, and practically no hydrogen at all (at $-190^\circ C$). H_2O , and CO_2 are still strongly sorbed, although also to a somewhat smaller degree than by all other

Discussion.

In general, the above results are in agreement with our assumption. The replacement of divalent by monovalent ions actually decreases the sorptive capacity of the crystals. The influence of the larger K^+ is more pronounced than that of the smaller Na^+ ions.

It is, however, difficult to interpret satisfactorily the details of the experimental results. The unchanged capacity for sorbing water and carbon dioxide indicates that space for sorption is not, or not essentially, decreased by the introduction of alkaline ions. The slightly smaller H_2O and CO_2 content of K-chabasite may be due to the space occupied by the K^+ -ions becoming unavailable for sorption. (The number of additional monovalent ions—about 0.8 mols. according to Table II.—is nearly equivalent to the decrease in the number of water molecules). This effect is, however, absent in the Na chabasite; and in the case of

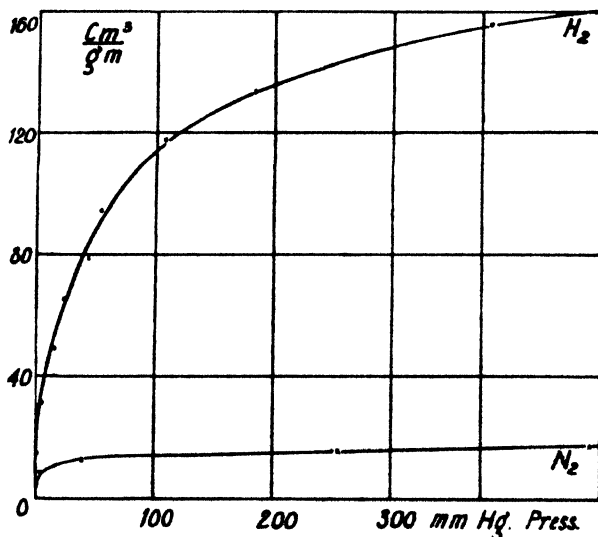


FIG. 6.—Sorption by sodium-chabasite at $-190^\circ C$.

K^+ it may also be due to an incomplete saturation, i.e. to a smaller sorption energy. In any case, the small difference in the space available for sorption cannot account for the strong differences observed in sorption experiments with H_2 and N_2 . They must be due to *energetical* conditions. The results obtained with the *potassium chabasite* are consistent with an

assumption that the sorption energy both for hydrogen and nitrogen is decreased in the relation of about 5 : 1 (as compared with calcium chabasite). The sorption energies for carbon dioxide and water are also decreased, but to a much smaller degree.

The most difficult to understand are the results with *sodium chabasite*, in which the initial sorption energy for hydrogen appears to be reduced only by a factor 0.7, whereas the sorption energy for N_2 is diminished roughly in a relation 3 : 1. Sodium chabasite can be described either as possessing an abnormally high sorptive capacity for hydrogen, or an especially low sorptive capacity for nitrogen (Fig. 6).

We may recall that the natural chabasite from Richmond (Victoria) which led to this investigation, had a sorptive capacity uniformly reduced (in the relation 3 : 1) for all the three gases H_2 , N_2 and CO_2 . This result illustrates the variety of the sorption effects occurring in alkali substituted chabasites.

Sorption Formulæ.

The experimental results described above are not sufficiently complete to be used for quantitative representation by sorption formulæ as was done with the sorption isothermals of the natural chabasite in Paper I. We can here, however, improve the theoretical treatment given in that paper. Two possible states of the molecules sorbed by chabasite were mentioned there: (a) that of a "gaseous" sorbate, with molecules freely moving about in the cavities of the crystal, and (b) that of a "solid" sorbate, with molecules fixed to definite crystallographical positions. The first picture does not exclude the existence of periodical variations in the potential, or of more or less high "potential barriers" in certain lattice positions, thus accounting for the slowness of diffusion of the sorbate. The second picture must account for the existence of diffusion by assuming accidental interchanges of molecules between adjoining sorption centres. In this way, the two extreme hypotheses converge towards an intermediary picture of a "partially fixed" sorbate, which is probably nearest to the truth.

The actual state of a given sorbate, however, may be nearer to the one of the two pictures. It is therefore useful to have sorption formulæ for both limiting cases.

(a) Gaseous Sorbate.—The formulæ for the distribution of molecules between a gas phase and a zeolite was given in Paper I. as follows:

$$\frac{N_a}{N_g} = \frac{(V_a - bN_a)}{V_g} e^{\phi/RT} \quad (1)$$

N_a is the number of molecules of the sorbate in the solid phase, N_g that in the gas phase, V_a the "sorption volume" of the crystal, b the volume required by a single molecule, V_g the volume of the gas phase, ϕ the sorption energy (per mol.). Supposing b to be independent of the degree of saturation, we may assume $V_a = bN_{\max.}$, where $N_{\max.}$ is the maximum number of molecules which can find place in the crystal. Hence

$$\frac{N_a}{N_g} = \frac{(N_{\max.} - N_a)b}{V_g} e^{\phi/RT} \quad (1')$$

For constant concentration of the sorbate $\left(\frac{N_a}{N_{\max.} - N_a} = \text{const.}\right)$ the following vapour pressure formula (3) is derived from (1)

$$\log_e p_{\text{atm.}} = -\frac{\phi}{RT} + \log_e T + \log \frac{N_g}{N_{\max.} - N_a} - \log_e N_A T_0 b \quad (2)$$

where N_A is the number of molecules in c.c. of the gas at $t = 0^\circ \text{C.}$ and $p = 1 \text{ atm.}$ ⁴

(b) Solid Sorbate.—The statement in Paper I. that "formula (1) holds also for the case of a fixed number of sorbing centres, b meaning in this case the volume of each centre and V_a that of all of them together" requires correction. The distribution of molecules between

⁴ M. H. Hey, (*Mineralogical Magazine*, 1935, 24, 99) derived, by kinetic considerations, a vapour pressure formula very similar to (2) (but with slightly different meaning of some constants). Some constants in his formulæ are, however, related to the special mechanism of evaporation and condensation which he uses for derivation—a result not in accordance with thermodynamics, which requires that a formula describing an equilibrium shall contain nothing about the mechanism by which this equilibrium is reached.

gas phase and a fixed number of sorption centres depends on the *number* of unoccupied centres only, and the notion of the "volume of a sorption centre" is an unnecessary complication. Moreover, law (1) does not apply unchanged to a distribution of this kind. In passing from the gaseous state into that of a *solid* sorbate, the molecules lose not only their potential energy of sorption ϕ but also their kinetic energy. The distribution law is therefore more complicated. The probability of finding a molecule in the gas phase (volume V_g , temperature T) is, according to quantum statistics :

$$P_{\text{gas}} = \int_{E=0}^{\infty} V_g \frac{4\sqrt{2\pi m^3} E^{\frac{1}{2}}}{h^3} e^{-E/kT} dE.$$

The probability of finding the molecule in the solid sorbate is :

$$P_{\text{solid}} = (N_{\text{max.}} - N_a) e^{\phi/RT}$$

and the distribution law is therefore

$$\frac{N_a}{N_g} = \frac{N_{\text{max.}} - N_a}{V_g} \frac{h^3 N_A^3}{(2\pi MRT)^{\frac{3}{2}}} e^{\phi/RT} \quad (3)$$

a formula which differs essentially from (1) by the occurrence of the factor $T^{\frac{3}{2}}$, and by the molecular weight M replacing the molecular volume b in the rôle of a characteristic constant of the sorbate.

The vapour pressure formula derived from (3) is :

$$\log_e p_{\text{atm.}} = -\frac{\phi}{RT} + \frac{5}{2} \log_e T + \log_e \frac{N_a}{N_{\text{max.}} - N_a} + \log_e \frac{(2\pi RM)^{\frac{3}{2}}}{h^3 N_A^4} \quad (4)$$

Equation (4) differs from the ordinary quantum theoretical vapour pressure formula of a homogeneous ideal solid body by the occurrence of the characteristic "saturation term"

$$\log \frac{N_a}{N_{\text{max.}} - N_a}$$

(c) Vibrating Sorbate Molecules.—Since the sorption energies are not greater than 30,000 Cals. per mol., the quanta corresponding to the vibrations of the molecules around their equilibrium positions must be of the order of 1000 Cals. (300 cm.^{-1}) or smaller and these vibrations are by no means "frozen" at temperatures above 100°abs. (which were used in most sorption experiments). The law of distribution of molecules between gas and sorbate is in this case :

$$\frac{N_a}{N_g} = \frac{(N_{\text{max.}} - N_a)}{V_g} \sum_v e^{-E_v/RT} \frac{h^3 N_A^3}{(2\pi MRT)^{\frac{3}{2}}} e^{\phi/RT} \quad (5)$$

and the corresponding vapour pressure formula :

$$\begin{aligned} \log_e p_{\text{atm.}} = & -\frac{\phi}{RT} + \frac{5}{2} \log_e T + \log_e \frac{N_a}{N_{\text{max.}} - N_a} \\ & - \log_e \sum_v e^{-E_v/RT} + \log_e \frac{(2\pi RM)^{\frac{3}{2}}}{h^3 N_A^4} \quad (6) \end{aligned}$$

In these formulæ, E_v is the vibrational energy (per mol.) corresponding to the state with the vibrational quantum number v .

(d) **Isothermals.**—From all the three formulæ (2), (4) and (6), we obtain the following isothermal equations:

$$\frac{N_a}{N_{\max} - N_a} = ap; \quad N_a = \frac{apN_{\max}}{1 + ap} (a = \text{const}) . \quad (7)$$

A law of this form must hold for the sorption isothermals independently of the "gaseous," "solid" or "semi-solid" state of the sorbate, provided only that ϕ is a constant independent of the saturation N_a/N_{\max} .

The experimental sorption isothermals of chabasite, however, never fulfil law (7). This shows clearly that the sorption energy is dependent on saturation. Two possibilities may be considered: the sorption energy may either decrease continuously with increasing sorption, or it may change in steps. In Paper I. we made the mistake of expecting that sudden changes of the sorption energy must reveal themselves by discontinuities or inflexions in the sorption isothermals. This is not true. If, for instance, the crystal contains two kinds of sorption centers, N_1 (with the energy ϕ_1), and N_2 (with the energy ϕ_2), then the distribution between gas phase and each set of centers will be independent of the existence of the second set and given by a formula of the kind (7). The total number of molecules in the sorbed state will be:

$$(N_a)_1 + (N_a)_2 = p \left(\frac{a_1(N_{\max})_1}{1 + a_1p} + \frac{a_2(N_{\max})_2}{1 + a_2p} \right) . \quad (8)$$

This equation represents a smooth function without any discontinuities or inflexions. Obviously, a continuous change of ϕ with N_a/N_{\max} may be expected to occur in the case of a "gaseous" or nearly gaseous sorbate, whereas the existence of a discrete set of values ϕ_1, ϕ_2, \dots is more characteristic of a "solid" sorbate with a number of different crystallographic positions occupied by the molecules of the sorbate.

(e) **Saturation.**—In the case of a fixed number of sorption centers, the number of molecules corresponding to the saturation state must be the same for all kinds of sorbates, or, alternatively, only a few widely separated saturation values may be found, forming a small whole number series. This may occur either in the case of larger molecules occupying two or more centres, or in the case of a particular set of centers being unavailable for some kind of sorbate. In the case of a gaseous sorbate, the saturation values may vary continuously according to the size and shape of the molecules.

In Paper I. we used formula (1) for the representation of the isothermals, considered ϕ as a continuous function of the concentration and extrapolated individual saturation values for all gases investigated. In doing so, we practically adopted the hypothesis of the "gaseous" sorbate.

After the appearance of that paper, it has been, however, suggested⁵ that chabasite possesses two crystallographical positions which are vacant in the dehydrated lattice. Under these circumstances, two different saturation values and two different sorption energies for each gas may be expected. Hey suggested that the saturation values extrapolated in our previous paper may be arranged in two groups—some being close to 330 c.c./gm. (corresponding to 12 molecules of sorbate per unit cell) and the others to about $\frac{1}{3}$ of this value. Fig. 8 in Paper I. shows that this interpretation is not incompatible with the experiments

⁵ See A. Tiselius, *Z. physik. Chemie*, 1935, **A**, 174, 401.

made with natural calcium chabasite. The results obtained with the substituted chabasites and illustrated by Figs. 2-5 in this paper are, however, more difficult to reconcile with this scheme. To interpret them would require much more than two different kinds of centers. Besides the saturation values 330 and 165 c.c., those lying in the neighbourhood of 80 c.c. and 20 c.c. are suggested by the slope of some curves.

By assuming 4 or more different kinds of positions, each having its own characteristic sorption energy, one has in hand enough independent constants to be able to represent all the experimental isothermals. A representation of this kind is, however, of no great value in the actual state of the experimental material available. Fuller investigations of the sorption equilibrium may, however, give, with the help of the above derived formulæ, information about the state of the sorbates under different conditions.

The experimental part of this paper forms one part of the dissertation presented by Mr. W. C. Wood to the Faculty of Science of the University of Göttingen. Results of an investigation of the electrical properties of zeolites, which were included in this dissertation, were communicated on a previous occasion.⁵

The experiments were carried out in the Minerological Institute of the University of Göttingen, to whose Director, Professor V. M. Goldschmidt (now is Oslo), we are highly indebted for his kind interest in this work and many valuable suggestions. We also thank Dr. E. Thilo for valuable advice in the analytical part of this work.

⁵ E. Rabinowitch and W. C. Wood, *Z. Elektrochemie*, 1933, **39**, 562.

THE ABSORPTION SPECTRUM OF AQUEOUS CHLORINE AND HYDROGEN PEROXIDE VAPOUR.

BY W. C. FERGUSON, L. SLOTIN AND D. W. G. STYLE.

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The extinction coefficients for gaseous chlorine have been accurately determined by v. Halban and Siedentopf¹ for the chief mercury arc lines, and Barratt and Stein² and Gillam and Morton³ have made measurements of the absorption of solutions of the gas in carbon tetrachloride, which show that the absorption spectrum in this solvent is approximately the same as that in the gaseous state.

The absorption of aqueous solutions have an especial interest on account of the thermal hydrolysis and photochemical reactivity of such solutions. According to E. S. Ssokolowa and P. I. Ssokolow⁴ the extinction coefficients of aqueous chlorine are, for the wave-length 436, 454, and 463 mμ, approximately the same as those of the gas. This is in agreement with the earlier measurements of Allmand, Cunliffe and Maddison,⁵ who concluded that within the limits of their, admittedly,

¹ *Z. physik. Chem.*, 1922, **103**, 513.

² *Proc. Roy. Soc., A*, 1929, **122**, 582.

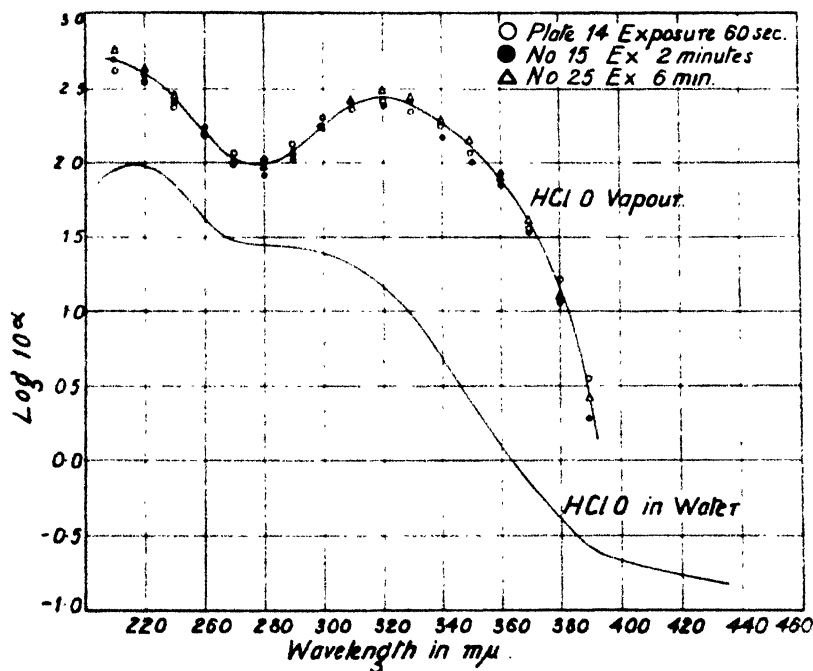
³ *J. Russ. Physic. Chem.*, 1930, **62**, 319.

⁴ *J. Chem. Soc.*, 1927, 655.

⁵ *Ibid.*, **124**, 604.

rather large experimental error there was no marked difference between the extinction coefficients of gaseous chlorine and its aqueous solution for the wave-lengths 436, 405, and 365 $m\mu$.

In the present work these measurements are repeated and extended so as to cover the whole spectrum between 420 and 220 $m\mu$. As, however, the thermal hydrolysis results in the production of hypochlorous and hydrochloric acids it was necessary to determine the magnitude of the corrections due to these substances. The degree of hydrolysis and consequently the concentrations of the acids present could be readily calculated from the values of the equilibrium constant given in Lewis and Randall's *Thermodynamics*, page 508. Owing to the very slight absorption of the chloride ion,⁶ no correction is necessary for the absorption of the hydrochloric acid. Hypochlorous acid on



the other hand absorbs considerably throughout the spectral region investigated.

As the existing measurements on hypochlorous acid were neither extensive nor accurate enough, it was necessary as a preliminary to determine its absorption spectrum.

Hypochlorous Acid.—The acid was prepared by distillation of a mixture of bleaching powder, boric acid and water under reduced pressure, the distillate being redistilled from silver sulphate in order to remove traces of chloride. The approximately 0.2 *M.* solutions so prepared were diluted as required.

For the absorption measurements a Judd-Lewis sector photometer in conjunction with a Hilger E.2 quartz spectrograph and an iron spark

⁶ Frommers and Menschik ; *Z. physik. Chem.*, 1930, 137, 439.

was used. The points of equal density in the photographs were determined visually. The absorption cells were made up of drilled glass blocks over the ground plane-parallel ends of which crystal quartz plates were clamped. Although no cement was used, leakage was insignificant. Various depths of solution between 5.0 and 0.1 cm. were used. The reflection and other light losses were balanced by cells of similar depth filled with water. Transmissions greater than 50 per cent. were not used in order to avoid errors due to small differences in the characteristics of the cells. The concentrations were determined iodimetrically.

The mean results of these measurements are shown in Fig. 1 in which logarithms of the decadic extinction coefficients are plotted against the wave-length. No dependence of the extinction coefficient upon the concentration could be detected within the concentration range of 0.017 — 0.15 *M*.

Chlorine Water.—For the preparation of the chlorine water both commercial chlorine taken direct from a cylinder of the liquefied gas and

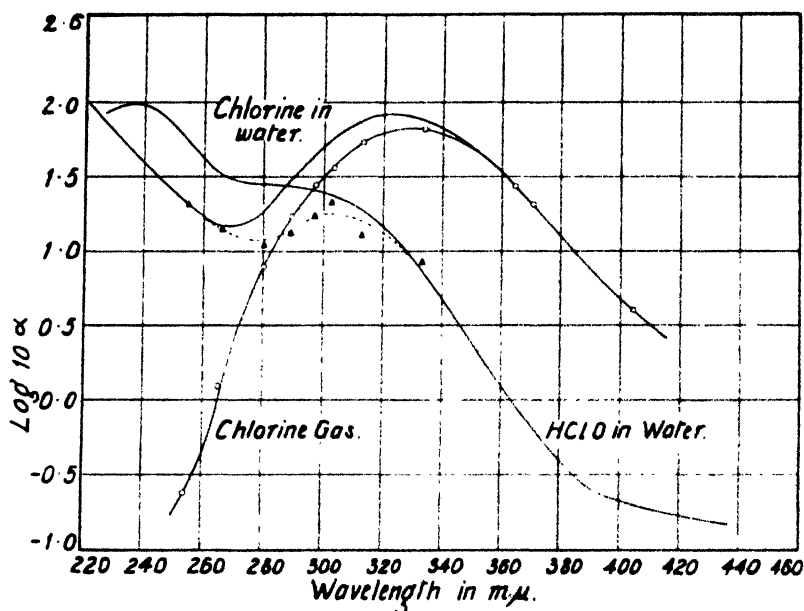


FIG. 2.

chlorine purified by washing with water, liquefaction and distillation were used. The purified chlorine gave somewhat lower values of the extinction coefficient particularly at shorter wave-lengths where the correction for the hypochlorous acid formed by the hydrolysis is of most importance.

In order to avoid concentration changes, the chlorine solutions were prepared by passing the chlorine through water contained in a special all-glass storage vessel. From this vessel the solution could be siphoned out either into the absorption cell or into a special pipette designed by Mr. H. N. Ridyard and K. W. Young for accurate measurements on chlorine solutions. The air replacing the chlorine water removed, passed through two bubblers containing solution of the same strength as that in the main vessel.

The concentrations of the chlorine-water was determined both immediately before and immediately after filling the absorption cell, the mean value being taken as that of the solution in the cell.

The extinction coefficients of the unhydrolysed chlorine were calculated from the expression

$$\log_{10} \frac{I_0}{I} = d(\alpha_{Cl_2}[Cl_2] + \alpha_{HOCl}[HOCl])$$

in which α_{Cl_2} and α_{HOCl} are the extinction coefficients of Cl_2 and $HOCl$ respectively, I_0 and I respectively the incident and transmitted light intensities, and d the thickness of the absorbing layer of solution.

As the degree of hydrolysis, and consequently the correction for the absorption of hydrochlorous acid increases with the dilution, concentrations of less than 0.04 *M.* could not be used for quantitative measurements. The results obtained with the purified chlorine are plotted in Fig. 2.

Since the absorption spectrums of aqueous hypochlorous acid might differ considerably from that of the vapour, and in particular since discontinuous absorption if it occurs could only be detected in the vapour phase, the absorption of the vapour was investigated. At the same time the absorption of hydrogen peroxide vapour was also redetermined as it seemed probable that the work of Urey, Dawsey and Rice⁷ was in error, since their results for aqueous solutions differ considerably from the concordant results of several other workers.⁸ No indication of any discontinuity in the absorption of hypochlorous acid vapour could be detected between 230 and 390 μ , using a Hilger E. 2 Spectrograph.

Hydrogen Peroxide and Hypochlorous Acid Vapours.—Since neither of these substances can be obtained at a high concentration in the vapour phase, it is necessary to employ a long absorption tube if the absorption measurements are to be reliable.

A translucent silica tube 10 metres in length and 2.5 cm. in diameter with fused on transparent end plates, heated electrically to about 45° C. was used. The hypochlorous acid vapour was obtained from aqueous solutions prepared by the method already described and the peroxide vapour from redistilled Merck's "Perhydrol."

To one end of the absorption tube B (Fig. 3) was sealed a quartz flask A, containing a solution of the vapour to be investigated. During absorption measurements the vapour was distilled through B into the liquid air trap E, a convenient pressure being maintained in B by the capillary D and control of the tap H. A "Hyvac" pump continually removed permanent gas. In order to measure the pressure in B a narrow bore lead was taken from one end of B to the manometer G. Peroxide vapour was prevented from reaching the manometric liquid by manganese dioxide heated to 100° C. contained in the bulb C, while the water vapour initially present or formed by the decomposition of the peroxide was frozen out in the trap F, so that only oxygen reached the manometer. With

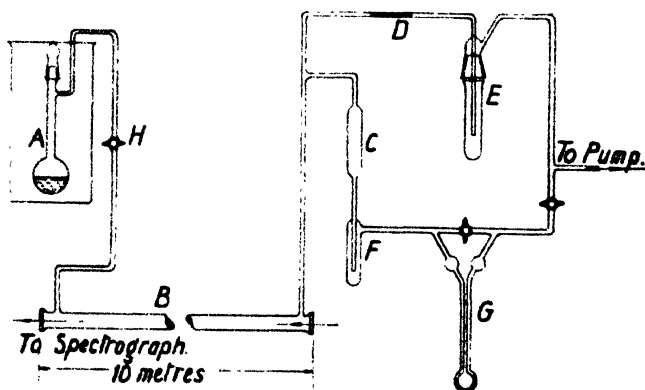


FIG. 3.

⁷ Urey, Dawsey and Rice : *J.A.C.S.*, 1929, **51**, 1371.

⁸ Henri and Wurmser : *C.R.*, 1913, **156**, 1012; Rieche and Lederle, *Ber.*, 1929, **62**, 2573; Allmand and Style, *J. Chem. Soc.*, 1930, 596.

hypochlorous acid, C was replaced by a capillary leak open to the atmosphere in order to supply the gas to operate the manometer.

After each exposure the condensate in the trap E was melted and the molal fraction of peroxide or hypochlorous acid determined by the usual analytical methods. The temperature and total pressure in the absorption tube being known, the concentrations of the absorbing vapours could be readily calculated. These lay between 1 and 4×10^{-5} gm. mols./litre with hypochlorous acid and between 5×10^{-5} and 5×10^{-6} with hydrogen peroxide.

A hydrogen discharge between stainless steel electrodes in a water-cooled silica tube served as the light source. Before entering the absorption tube the light was rendered approximately parallel by the sector box lens system of a dismantled Judd-Lewis sector photometer. The absorption of the peroxide vapour was determined by taking pairs of photographs with the same time of exposure without moving the photo-

graphic plate but with different adjacent portions of the slit of the spectrograph exposed, one with the tube evacuated (the tap H being closed) and the other with peroxide vapour flowing through the tube and the sector adjusted to give the maximum transmission. The match points were determined visually. The accuracy of this method was checked by determining the extinction coefficients of chlorine, values within 5 per cent.

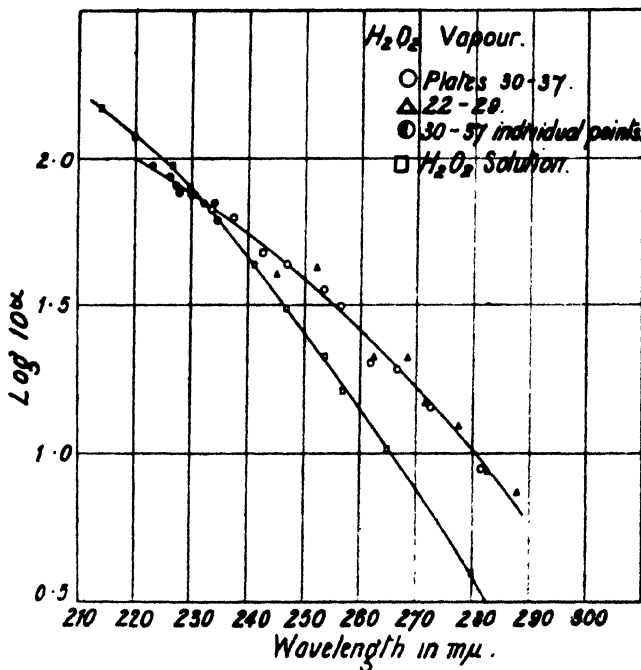


FIG. 4.

of those given by v. Halban and Siedentopf being obtained.

The instability of hypochlorous acid and the weak absorption usually obtained with it necessitated the adoption of a different procedure with this substance.

A calibration series of spectra was photographed through the evacuated tube with constant time of exposure, but with the sector adjusted to give different transmissions. Photographs were then taken with the same exposure but with hypochlorous acid vapour flowing through the tube and the sector set to give the maximum transmission. The absorption of the vapour at a number of wave-lengths was then found by comparing the densities of the photographs taken through the vapour with the calibration series by means of a recording micro-photometer.

The results for hydrogen peroxide are shown in Fig. 4 and the results from a few representative plates obtained with hypochlorous acid in Fig. 1.

Discussion.

Although, as can be seen from the scattering of the extinction coefficients of gaseous hypochlorous acid, no great accuracy can be claimed, there can be no doubt that there is a very considerable difference between the absorption of this substance in the vapour and dissolved states. This difference cannot be ascribed to either chlorine monoxide or chlorine dioxide, since the absorption in no way resembles that of the monoxide,⁹ and the very easily detectable bands of the dioxide were entirely absent from all plates used for measurement. The dioxide bands did, however, sometimes appear if the hypochlorous acid solution was not freshly prepared. The very marked depression of the transition probability on passing from the vapour to the dissolved state is rather exceptional since chlorine is scarcely affected at the longer wave-lengths, and with hydrogen peroxide the effect of dissolution seems to be to simultaneously increase the maximum absorption and make the band narrower. The mean time of contact of the vapour with the heated tube was only of the order of 5 seconds, but no attempt was made to keep it constant from exposure to exposure, so that the difference between solution and vapour can scarcely be accounted for by assuming that some 90 per cent. of the vapour decomposed during its passage through the absorption tube. The concentration of the condensate was moreover too great to allow of the assumption that any extensive decomposition had occurred. The large effect of the solvent may perhaps be due to the asymmetry of the hypochlorous acid molecule, and its consequent considerable interaction with the water dipoles.

The dissociation products which might be obtained from the hypochlorous acid molecule are: $\text{OH} + \text{Cl}$ (either or both being excited), requiring 55 Cals. for unexcited products, $\text{HCl} + \text{O}({}^3P)$, requiring 57 Cals., $\text{HCl} + \text{O}({}^1D)$ requiring 102 Cals. and $\text{H} + \text{ClO}$ requiring 109 Cals., if the heat solution of hypochlorous acid is taken as 10 Cals. and the heat of dissociation of ClO is 50 Cals.¹⁰ Either of the two first of these might be produced by light absorption in the longer wave-length band. The failure to detect the presence of any discontinuity in the absorption even at the wave-length where the extinction coefficient is a minimum ($\lambda \sim 277 \text{ m}\mu$) excludes any process requiring more than 102 Cals. from responsibility for the absorption at shorter wave-lengths. Dissociation into $\text{H} + \text{ClO}$ can thus be left out of account unless this band is not simple, as it appears to be. $\text{HCl} + \text{O}({}^1D)$ remain, however, just possible.

The maximum of the second band lies outside the region covered by these measurements, but from the general trend of the curve might be expected to occur at about $210 \text{ m}\mu$, giving about 47 Cals. as the energy separation of the two maxima. This approximates to the difference between the two oxygen terms ${}^1D - {}^3P = 45$ Cals. Notwithstanding this apparent agreement the available evidence scarcely justifies the assignment of any one of the three possible dissociation processes to either band.

The effect of water upon the absorption of chlorine is zero within the experimental error for wave-lengths between 350 and $420 \text{ m}\mu$.

⁹ Goodeve and Wallace, *Trans. Faraday Soc.*, 1930, **26**, 254. Also ref. 10.

¹⁰ Finkelburg, Schumacher and Stieger, *Z. physik. Chem., B*, 1931, **15**, 127.

At shorter wave-lengths, however, there is an increase in the absorption culminating in the appearance of a new band below $270\text{ m}\mu$, the maximum of which is not attained within the limits of our measurements.

A similar but more intense change in the absorption has been found on dissolution in strong aqueous hydrochloric acid (4 to 10 molar), when a very intense absorption sets in below $290\text{ m}\mu$, the absorption at longer wave-lengths remaining meanwhile similar to that of the gas. If the hydrochloric acid contained hydrobromic acid the long wave-length maximum shifted to $380\text{ m}\mu$, the position of the maximum of bromine chloride in carbon tetrachloride.¹¹ According to the data of Forbes and Fuoss¹² the chlorine would have reacted almost completely to form bromine chloride under our conditions. The absorption obtained with the solutions containing hydrobromic acid was very similar to that of BrCl_2^- excepting that the absorption at shorter wave-lengths found by us was much stronger than that reported by Gilbert, Goldstein and Lowry.¹³ This difference is readily accounted for if the complex ion is considerably dissociated if a large excess of chloride ion is not present.

By analogy the ion Cl_2^- is presumably responsible for the absorption obtained with chlorine in hydrochloric acid solution, and further, the difference between the absorption of gaseous chlorine and its aqueous solution (which is indicated by the dotted curve of Fig. 2) may be ascribed to the ion Cl_2OH^- or perhaps the molecule HCl_2OH . Though possibly merely a coincidence it is worth noting that this difference rather closely resembles the absorption of hypochlorous acid vapour (Fig. 1).

In view of the experimental methods employed, it would seem that the present values of the extinction coefficients of hydrogen peroxide are to be preferred to those of Urey, Dawsey and Rice.

Summary.

The absorption spectra of aqueous chlorine and hypochlorous acid solutions and of the vapours of hypochlorous acid and hydrogen peroxide have been investigated.

The interpretation of the observations is discussed.

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¹¹ Gillam and Morton, *Proc. Roy. Soc., A*, 1929, **124**, 604.

¹² Forbes and Fuoss, *J.A.C.S.*, 1927, **49**, 142.

¹³ *J. Chem. Soc.*, 1931, 1092.

THE PROTON AFFINITIES OF SPARINGLY SOLUBLE BASES: BENZIDINE.

BY E. B. R. PRIDEAUX AND J. H. PARKINSON.

Received 23rd April, 1936.

The dissociation constants of bases having solubilities below about 0.001 mols./litre cannot be determined by the ordinary methods with the same accuracy as those of soluble bases, on account of the low concentrations and consequent lack of hydrogen ion regulating power, *e.g.*, of the equimolecular free base, salt mixtures. The first constant of benzdine was, however, determined by Pring¹ who measured $[H^+]$ of the 0.001 *N.* hydrochloride and base (*a*) by the quinhydrone (*b*) by the hydrogen, electrode and (*c*) colorimetrically, and found (classical) basic dissociation constants $k_B = 1.7 \times 10^{-9}$, 1.45×10^{-9} and 1.58×10^{-9} respectively. If we take the mean value of 1.58×10^{-9} and express the basic constant as a hydrolysis constant k_W/k_B , which is also an apparent acidic constant k_H , then pk_H or $pk_1 = 5.2$.

Since $1/k$ represents the proton affinity of the base which is given by $[BH^+]/[B][H^+]$, the magnitude of pk_1 is a measure of the affinity of the base for the first proton.

In order to obtain a mean value of this constant (which is often found to vary slightly with the degree of neutralisation, a number of points on each side of the half-equivalence point have been obtained, and corrected by the equation :

$$pk_1 = p_H + \log \frac{[BH^+] - [H^+]}{[B] + [H^+]}$$

10 c.c. of an *M*/2000 solution of the base containing 0.092 g./litre were treated with 0.01176 *N* HCl, 0.135 to 0.335 c.c., added from a micro-burette, and the p_H values determined by matching with B.D.H. universal indicator in a test-tube comparator. Mean $pk_1 = 4.97$.

The hydrolysis of *M*/2000 BHCl was investigated with B.D.H. universal, bromocresol blue and bromophenol blue, indicators. The mean p_H was 4.3. Applying the usual equation :

$$p_H = 7 - \frac{1}{2}pk_B - \frac{1}{2} \log C \quad . \quad . \quad . \quad . \quad (2)$$

we find, $pk_B = 8.9$, $pk_1 = 5.1$.

Although this method apparently gives a correct result, yet it must be noted that the simple hydrolysis equation is not really applicable, since the second constant has an exponent which only differs from that of the first by little more than a unit. The p_H of the first equivalence point is intermediate between pk_1 and pk_2 , so that the general equation of a diacid base should be used, which may be expressed in the form :

$$[H^+]^2 = \frac{k_1 k_2 C}{k_1 - C}$$

in which k_1 , k_2 are the apparent acidic constants. Taking negative exponents of $[H^+]$, k_1 and k_2 , we obtain :

$$p_H = \frac{1}{2}(pk_1 + pk_2) \quad . \quad . \quad . \quad . \quad (3)$$

¹ *Trans. Faraday Soc.*, 1924, 19, 705.

Inserting the value of $pk_1 = 5.0$, then $pk_2 = 3.4$, which is 0.4 units less than that found experimentally.

The second constant was determined by adding 0.0294 *N* NaOH from a microburette to 10 c.c. of the 0.005 *M* base dihydrochloride in the presence of dimethylaminoazobenzene and methyl orange. The equation contains a hydrolysis correction which is rather high :

$$pk_2 = p_H + \log \frac{[BH_2^{**}] - [H^*]}{[BH^*] + [H^*]} \quad (4)$$

in which $[BH]$ is the uncorrected amount of monohydrochloride corresponding to the addition of x c.c. of alkali. The calculated pk_2 varied between 3.6 and 3.9, the mean of 10 results being 3.75.

As already remarked, this exponent is too high to yield the experimental equivalence point of monacid base. While, however, the first constant was determined in solutions so dilute that no correction is needed for total "ionic strength," the second was determined in more concentrated solutions, and should be corrected by some function of C , which would probably give a lower value to the ideal or limiting pk_2 .

Dissociation Constants in Aqueous-Alcoholic Solutions.

The constants in methyl alcohol, 50 per cent., were found by Kuhn and Zumstein,² who measured the E.M.F. of the combination: H_2PtB , $BHCl$ 3.5 *N* KCl , 3.5 *N* KCl , $HgCl$ Hg at 20°. The normal potential of the calomel 3.5 *N* potassium chloride was taken as 250 mv. The results are expressed by the general equations corrected for activities of BH and BH_2 at the ionic concentrations.

$$pk_1 = pa_H - \log [B]/[BH^*] - 0.43\sqrt{C}$$

$$pk_2 = pa_H - \log \frac{[BH^*] + [H^*]}{[BH_2^{**}] - [H^*]} - 1.28\sqrt{C}.$$

In these solutions, $pk_1 = 4.89$, $pk_2 = 3.74$.

The pk values of several bases in mixtures of ethyl alcohol and water have been obtained electrometrically, and the results extrapolated to zero concentration of alcohol.³

Experimental.—Pure benzidine (0.3683 g.) was dissolved in 100 c.c. of dry alcohol. 5 c.c. portions of this solution were made to 50 c.c. by adding appropriate amounts of standard hydrochloric acid, water and alcohol, in order to give a series of solutions containing 10 up to 70 per cent. of alcohol and 0.04 molar half-neutralised base. The E.M.F. at 20° of the chain :

H_2Pt alcoholic base — HCl saturated KCl , agar sat. KCl

$HgCl$ Hg gave $p_H = \frac{E - E_0}{0.058}$, in which $E_0 = 246.4$ mv.

The results are shown graphically in Figs.

For the *monacid* base pk_1 is 4.60 in 70 per cent. and 4.99 in 15 per cent. alcohol, extrapolated value, 5.09.

For the *diacid* base, pk_2 is 3.42 in 60 per cent. alcohol and 3.67 in 10 per cent., extrapolated value, 3.79.

² *Ber.*, 1920, **59**, 488.

³ Michaelis and Mitzutani, *Z. physik. Chem.*, 116, 135; Hall and Sprinkle, *J. Amer. Chem. Soc.*, 1932, **54**, 3469.

Systems Containing Solid Base, Relation between Dissociation and Solubility:

Heterogeneous systems would seem to be particularly suitable for determining constants of very slightly soluble bases, since the solutions are well buffered as well as dilute. It is first necessary to develop the appropriate equations.

Solid Base present.—As before, the free uncharged base will be represented by B , the univalent kation by BH^+ and the divalent by BH^{++} . The concentrations of the various ions are regulated by the dissociation constant, k_B , the solubility product of the base:

$$[BH^+][OH^-] = k_B B = L_B \quad (5)$$

and, if solid salt is also present, by its solubility product:

$$[BH^+][Cl^-] = L_S \quad (6)$$

From electrical neutrality:

$$[BH^+] = [Cl^-] + \frac{k_W}{[H^+]} - [H^+] \quad (7)$$

The solutions are all acid, so that:

$$[BH^+] = [Cl^-] - [H^+] \quad (8)$$

$[Cl^-]$ can be calculated or obtained by titration, hence L_B from equation (5). In order to determine $k_B = \frac{[BH^+]K_W}{[B][H^+]}$, it is necessary to determine also B the concentration of undissociated base, which is practically equal to the solubility in pure water.

Solid Base and Solid Salt present.—In equation (7) substitute values of $[Cl^-]$ from (6), $[OH^-]$ from (5) and $[H^+] = \frac{[BH^+] \times K_W}{L_B}$ and obtain:

$$[BH^+] = \left\{ \frac{L_B(L_S + L_B)}{L_B + k_W} \right\}^{\frac{1}{2}} \quad (9)$$

The results showed that L_B can be neglected in comparison with L_S and therefore:

$$[BH^+] = \left\{ \frac{L_B L_S}{L_B + k_W} \right\}^{\frac{1}{2}} \quad (10)$$

These express the conclusion that the saturated solutions maintain constant concentrations of the hydrogen and other ions.

Experimental.—Solubility was determined by saturating a large volume of water with the base at 30° C. then cooling to and maintaining at 25°. 250 c.c. were extracted successively with 15 c.c. of chloroform. A blank experiment had shown that extraction was complete; the residual aqueous part gave no blue colour with a few drops of potassium dichromate solution, and therefore contained less than 1 in 50,000 of base. Evaporation of the united extracts showed a solubility of 0.0916 g./litre.

Saturated benzidine solutions in portions of 25 c.c. were treated with 0.2 g. of the solid base, and then with 1.3 to 3.5 c.c. of 0.09173 N HCl. A constant p_H of 4.3 was registered with bromocresol green in a Lovibond disc comparator.

100 c.c. portions of a saturated solution containing solid base were treated with varying amounts of 0.1 N HCl, shaken vigorously and allowed

to stand for a week, when the constancy of $p_H = 4.3$ was verified. The chloride ion was determined by thiocyanate titration, and was 6.37 to 6.42×10^{-3} g. ions per litre as 8 to 15 c.c. of the hydrochloric acid were added to 30 c.c. of the base solution.

From the values of $[BH^+]$, $[H^+]$ and $[B]$ obtained as above, the value of pk_B was found and is expressed as $pk_1 = 5.23$.

Solubility product of base,

$$L_B = k_B B = 1.72 \times 10^{-9} \times 7.24 \times 10^{-4} = 1.25 \times 10^{-12}.$$

Solubility product of monohydrochloride,

$$[BH^+][Cl^-] = 6.37 \times 10^{-3} \times 6.4 \times 10^{-4} = 4.08 \times 10^{-6}.$$

Summary of Affinity Constants ($k_w = 1.10 \cdot 10^{-14}$).

Method and Workers.	$k_B \times 10^9$.	pk_1 .	pk_2 .
Pring.—Electrometric and colorimetric	1.58	5.199	—
Colorimetric	1.25	5.097	3.61
Authors—Electrometric extrapolated	—	5.09	3.79
Heterogeneous system	1.74	5.23	—

Conclusions have been drawn from the magnitude of these affinity constants as to the structure of the molecule and the nature of the diphenyl linkage. These will be reserved for a later communication in which it is hoped to supply some hitherto undetermined constants of bases belonging to this class.

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THE INFLUENCE OF ULTRASONIC WAVES ON GELS.

BY H. FREUNDLICH AND K. SÖLLNER.

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This paper deals with the mechanism of the influence of ultrasonic waves on thixotropic gels and with their peptising effect in general.

1. The Liquefaction of Thixotropic Gels.

Some years ago¹ it was reported that thixotropic hydrogels (e.g. those of iron and aluminium oxides, bentonite, barium malonate) and several organo-gels are readily rendered fluid when irradiated with ultrasonic waves of high intensity for several seconds, the time of spontaneous solidification being the same as after vehement shaking. It was proved that this liquefaction is not due to thermal effects (which, after so short an irradiation, are small), as these gels have no tendency to soften or melt when moderately heated; indeed iron and aluminium oxides spontaneously solidify more rapidly at higher temperatures.²

¹ H. Freundlich, *Kapillarchemie* 4, *Auflage*, II. Bd. 1932, p. 616; H. Freundlich, F. Rogowski and K. Söllner, *Z. physik. Chem., A*, 1932, 160, 469; *Kolloid-Beihfte*, 1933, 37, 223; N. Marinesco, *C.R.*, 1932, 194, 1824.

² A. Szegevari and E. Schalek, *Koll. Z.*, 1923, 33, 326; H. Freundlich, F. Rogowski, and K. Söllner, *Kolloid-Beihfte*.¹

The liquefaction of gels contained in test tubes commences at the interface gel/air, the upper parts becoming liquid at once when irradiated with high energy. With iron oxide gels the process of liquefaction may easily be observed, as the colour of the gel turns to a much darker brown. The liquefied parts move rapidly and drops are thrown out forcibly from the surface. From the very start of the irradiation the whole gels shows brown spots, having a marbled appearance and on longer irradiation the amount of liquid increases, until the whole mass has become liquid.

The importance of the gel/air interfaces in the process of liquefaction may be strikingly demonstrated with transparent aluminium oxide gels,³ on shaking which, air-bubbles may be distributed throughout the whole mass. The creaming-up of these bubbles stops when the sol reverts to a gel, but the latter then contains numerous air-bubbles. When irradiated (preferably with not too high an energy) the bubbles move upwards, coalescing more or less and stopping at once when the irradiation ceases.⁴ Their movement is particularly strong where the oil fountain touches the test tube. In this way air-bubbles may be expelled from the gel, the latter not being rendered wholly fluid; this becomes evident on turning the test tube upside down. Only a thin layer of gel round the bubbles is liquefied, and through this the latter move upwards. Sometimes under these conditions the bubbles tend to form stationary wave patterns.^{5, 6}

When a test tube containing a thixotropic gel is turned upside down and then dipped into the oil fountain the gel does not fall down as a lump, but is rendered liquid at the lower surface; the liquid then runs down the walls of the tube and liquefaction proceeds on the surface until the whole mass is liquid.

In a previous paper a mechanism of emulsification by ultrasonic waves was suggested⁷ and it seemed worth while to investigate, how far the liquefaction of gels may be explained in the same manner.

It was shown that emulsification in oil/water systems is due to cavitation or more correctly to the vehement collapse of cavities. These cavities form when the liquid is unduly stretched during the expansion phases of the sound waves; if an external force (e.g. an external gas pressure) causes these cavities to collapse, violent mechanical processes such as emulsification occur.

This mechanism holds also for the liquefaction of gels; if liquefaction ceases when cavitation can no longer be effective, it must be attributed to cavitation.

Effective cavitation may be prevented,⁷ either by experimenting *in vacuo* so that no external force acts upon the cavities to cause them to collapse, or by applying such a high external pressure that no cavities are formed. Under neither of these conditions do ultrasonics render thixotropic gels fluid.

Experiments *in vacuo*.

Two samples of thixotropic iron oxide sol, having the same time of solidification when liquefied by shaking, were sealed in test tubes, the one (a) under normal pressure and saturated with air, the other (b) *in*

³ H. Freundlich, F. Rogowski and K. Söllner.¹

⁴ See Fig. 3 on page 236 *Kolloid-Beihfte*, 1933, 37.

⁵ E. Newton Harvey, *Biol. Bull.*, 1930, 59, 306; K. Söllner and C. Bondy, *Trans. Faraday Soc.*, 1936, 32, 616.

⁶ Solid particles also move in these gels on irradiation, but very much more slowly. If somewhat small they form stationary wave patterns under suitable conditions; if too big and too heavy, the radiation drives them to and fro, thus liquefying the gel around them slowly till they sink down in course of time.

⁷ C. Bondy and K. Söllner, *Trans. Faraday Soc.*, 1935, 31, 835.

vacuo after careful degassing. When exposed to ultrasonic waves of moderate energy, tube (a) readily liquefied, starting mainly from the top; tube (b) hardly changed, a thin layer only, at the surface being somewhat disturbed after a long time.

With very high energies drops of the gel were torn off and thrown upwards; an occasional small brown (liquefied) spot appeared also in some samples *in vacuo*, as it is difficult to make the gel absolutely gas-free, but even after prolonged irradiation only the top layer of the gel is at all disturbed, its "viscosity" still being obviously very high; the gel as a whole being unaffected. The tearing away of drops from the surface is always observed in the oil fountain over the vibrating quartz plate.* With the air-saturated gel, liquefaction was effected very rapidly.

When these experiments are performed in long tubes⁹ the results are still more pronounced. Only a slight surface movement is observed *in vacuo*, but with the air-saturated gel liquefaction always occurs (where in the emulsification experiments emulsification was seen), preferably at the top and secondly where the oil fountain touches the glass, the intermediate part being liquefied only after prolonged irradiation with high energy.

A more or less regular structure—dark brown/yellowish brown—is often observed, reminding one of the stationary wave patterns previously described.⁹ Effective cavities may to some extent be formed here also in the middle part of the tube; occasionally some of the darker spots grow rapidly, and then a gas bubble (due to degassing) will always be seen moving about in a liquefied zone, just as in the case of aluminium oxide gel, where, in the absence of formation of stationary waves in short columns, gas bubbles are driven to the surface, owing partially to radiation pressure, partially to their buoyancy.

Experiments under gas pressure were also carried out in long tubes, the external pressure of compressed gas being applied from a cylinder of compressed air. On irradiating now, even with high energy, nothing happens, except a slight movement of the meniscus; this does not cause true liquefaction, except perhaps in a thin upper layer. After prolonged irradiation this upper layer becomes slowly saturated with gas and liquefaction takes place in a narrow zone, the bulk of the gel being absolutely unaffected. When the pressure is turned off, liquefaction begins at once, cavitation now being possible.

These experiments show that the liquefaction of thixotropic gels occurs under exactly the same conditions as where emulsification is observed, *i.e.*, when cavitation (as defined in an earlier paper) is possible. Without cavitation the sound waves cannot even destroy the very weak structure of thixotropic gels.

These experiments show also that the particles of the gels investigated are too small to scatter any appreciable energy, since otherwise stationary wave patterns⁹ ought to appear; the gel behaves as a homogeneous medium.¹⁰ Foreign particles, *e.g.*, of quartz of several μ diameter, which are big enough to scatter sufficient energy to be affected individually, form stationary wave patterns in these gels just as in liquids.¹¹

* W. R. Wood and A. L. Loomis, *Phil. Mag.*, (7) 1927, 4, 417.

⁹ K. Söllner and C. Bondy, *l.*

¹⁰ Some phenomena observed in gel-like systems with particles large enough to be moved individually by the sound waves will be described shortly.

¹¹ The velocity of sound in these gels is nearly the same as in the medium of dispersion.

2. The Peptising Action of Ultrasonics.

In the peptisation of gels by ultrasonics¹² exactly the same result is obtained: neither *in vacuo* nor under a sufficiently high external pressure (so long as the system is not saturated with gas) is peptisation observed.

A sheet of commercial gelatine was rolled together and pushed to the bottom of a test tube, so that it could not be moved by the radiation pressure, when irradiated; then water was added. Three samples were thus prepared: the first (a) was left in that condition, the second (b) was carefully degassed and sealed off, and the third (c) was partially degassed to remove at least all gas bubbles adhering to the gelatine and then connected (with a high column of water on the top) to a cylinder of compressed gas, under a pressure of several atmospheres.

The three tubes were irradiated with medium energy; the gelatine foil in tube (a) started to collapse after 10 to 20 seconds, formed a voluminous clod, and was peptised entirely after about 40 to 60 seconds, the whole process being more rapid with higher energies. In the other two tubes, even after several minutes of irradiation and on applying high energy, the gelatine foils were quite stiff and unaffected, the water remaining quite clear.

Obviously the rate of swelling of suitable substances is much increased when peptisation occurs on irradiation.

Substantially the same result was obtained with many other substances, *e.g.* glue, rubber in different organic liquids, aluminium oxide in dilute HCl, so long as the adherent and enclosed gas is removed, when experimenting *in vacuo* or under pressure, a condition not always too readily fulfilled in the case of gels.

When combining the above facts with the results of many earlier investigations,¹³ one may conclude that all the destructive and disruptive effects in non-metallic systems (also in biological systems) reported by many authors must be attributed to cavitation, as defined in an earlier paper.⁷

Mention may also be made of two further points of importance in the peptisation of gels: the vigorous movement to be seen in two-phase systems when irradiated, and the heat developed.

The movement of suspended particles and the stirring effects due to large interfaces in heterogeneous systems were described in an earlier paper⁹ and the results obtained there may be applied accordingly to the peptisation.

When a liquid is irradiated, heat is always developed, particularly in the presence of large interfaces.¹² This is due partly to the absorption of sound energy (most pronouncedly with very viscous liquids, *e.g.* glycerol), but much sound energy is scattered and thus transformed into heat by interfaces. It seems, however, that cavitation also may play an important rôle.¹⁴ This question still needs more thorough investigation, specially as to how the occurrence of cavitation depends upon the presence of interfaces.

¹² W. R. Wood and A. L. Loomis; ⁹ H. Freundlich, F. Rogowski and K. Söllner, *Kolloid-Beihfte*.¹

¹³ *E.g.* E. Newton Harvey; ⁸ C. Bondy and K. Söllner.⁷

¹⁴ This seems to be correlated with the well-known fact that the propagation of sound is much feebler in liquids containing gas, than in gas-free ones.

Summary:

The liquefaction of thixotropic gels and the peptisation of gels in general by ultrasonic waves are due to the same effect as emulsification in non-metallic systems, *i.e.* they are due to cavitation. If the latter is prevented, either by external pressure or by experimenting *in vacuo*, no liquefaction and no peptisation is observed, when irradiating with ultrasonics.

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ON A MODE OF ACTION OF SOLVENTS ON CHEMICAL REACTION VELOCITY.

BY C. N. HINSHELWOOD.

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Two atoms combine stably only in ternary collisions, the rate being determined by the removal of energy from the product. If the rate is written $PZe^{-E/RT}$, P , though not E , will vary widely with the efficiency of the final deactivating collision.

This may apply to more complex association reactions, and efficiency of energy removal is, in principle at least, one of the factors concerned in solvent effects.

In a reversible reaction $XY = X + Y$, $[XY]/[X][Y] = K$ at equilibrium. In the gas phase the dissociation reaction is frequently of an order between the first and the second, the rate being $k_1[XY][M]/\{1 + (k_2/k_3)[M]\}$ where $[M]$ is the concentration of that species which activates XY by collision. Equally commonly, therefore, the association rate must be $k_1K[X][Y][M]/\{1 + (k_2/k_3)[M]\}$, to give the correct equilibrium constant. The direct derivation of this expression assumes the collision of X and Y to give an activated molecule which may either relapse to X and Y at a rate k_2a , or be deactivated by collisions to give a product at a rate $k_3a[M]$. Then

$$k_1'[X][Y] - k_2a[M] - k_3a = 0,$$

whence rate $= k_3a[M] = (k_2k_1'/k_3)[X][Y][M]\{1 + (k_2/k_3)[M]\}$.

When $(k_2/k_3)[M]$ is great compared with unity, the rate becomes independent of $[M]$ and k_2 : otherwise the rate depends upon the removal of energy from the product.

In a reaction in solution dependence on $[M]$ would not be evident, since M would be the solvent and $[M]$ constant. The rate might nevertheless be determined by the deactivation of the product by solvent molecules. At first sight $(k_2/k_3)[M]$ might be supposed always great compared with unity. This, however, is not necessary: $[M]$ is always great, but k_2 might be correspondingly small. The studies of Eucken¹ on the variation of the velocity of sound with frequency have shown that on the average many thousands of collisions may be necessary

¹ Eucken and Jaacks, *Z. physikal. Chem.*, B, 1935, 30, 85.

before a quantum of vibrational energy is converted into translational energy, and that the facility of transfer from molecule to molecule varies very widely. For example, 47,000 collisions occur before a molecule of carbon dioxide gains or loses a quantum of vibrational energy, while 630 are necessary for a molecule of hydrogen to remove a vibrational quantum from nitrous oxide. Transfer is extremely difficult except when the two colliding molecules exert strong specific forces on one another in virtue of dipoles, ionic charges or unsaturated valencies.

When the action of the solvent depends upon this mechanism we should expect:

(1) The value of P will vary widely from solvent to solvent. In favourable circumstances it would be possible to find a series of solvents in which changes in the velocity of a given reaction depended almost entirely on P . Simultaneous changes in E by different mechanisms are not precluded in general.

(2) In a reaction where a highly polar association product is formed, *e.g.*, in quaternary ammonium salt formation, the Eucken principle suggests that the energy could be most effectively removed from the ionised linkage by a molecule capable of exerting strong forces on it. Thus some rough functional relation between P and the dipole moment of the solvent might exist.

(3) For a very inert solvent $k_2[M]$ might be so small that one of the reactants or the product would have to play the part of the deactivating third body. Thus the reaction might become kinetically of a higher order than the second in the inert solvent.

(4) Increase of pressure, in virtue simply of the increased solvent collision number, could cause a considerable increase in P .

(5) Small additions of an active to an inactive solvent would bring about a *linear* increase in rate.

With regard to (1), the rather wide variation of P with solvent is evident from data already available in the literature, as for example in the work of Grimm, Ruf and Wolff² on the combination of triethylamine and ethyl iodide. The effect of the solvent on P is still more clearly shown in the reaction of pyridine and methyl iodide³ where it also appears that any correlation between the dipole moment of the solvent and the reaction rate is by way of P and not by way of E . This might be taken as an example of (2).

Examples of (3) are found. The reaction between benzoyl chloride and aniline is bimolecular in benzene, but in hexane, which is very much more inert, it shows marked autocatalysis by the reaction product. The influence of dilution is also quite anomalous, corresponding to a reaction order more nearly of three than of two.⁴ The same autocatalytic effect of the polar product is found in the methyl iodide-pyridine reaction in inert solvents, and an anomalous dilution effect with *m*-nitraniline and benzoyl chloride in carbon tetrachloride.⁵

(4) is exemplified by the marked increase in P found by Gibson, Fawcett and Perrin⁶ for the reaction between ethyl iodide and pyridine in acetone, where the increase of P between one and 8500 atmospheres is of the order of 1000 times, the increase of reaction rate with pressure occurring in spite of an appreciable increase in the activation energy.

² *Z. physikal. Chem.*, **B**, 1931, **13**, 299.

³ Unpublished experiments of N. J. T. Pickles.

⁴ Grant and Hinshelwood, *J. Chem. Soc.*, 1933, 1351.

⁵ *Proc. Roy. Soc., A*, 1935, **150**, 223.

(5) is exemplified by the addition of nitrobenzene to benzene in which the reaction of benzoyl chloride and aniline occurs.⁶ There is an increase in velocity proportional to the concentration of the two reactants and to that of the nitrobenzene.

It is not suggested that the removal of energy by the solvent molecules is a rate determining factor in general. All the examples quoted are of reactions where a polar salt is formed, and which show about the smallest values of P ever found. All the individual observations could be given alternative explanations, yet, taken together in the light of general considerations about the specificity of energy transfer, they lend some degree of significance to the question whether this function of the solvent has hitherto been taken fully enough into account. Those conditions where it is likely to be of importance are where there is difficulty about the dissipation of the activation energy into parts of the molecule remote from the active centre. There is evidence that such resistance to internal energy conversion plays a part in other kinetic phenomena.⁷

⁶ Williams and Hinshelwood, *J. Chem. Soc.*, 1934, 1079.

⁷ Cf. *Proc. Roy. Soc., A*, 1934, 146, 239.

REVIEW OF BOOK.

The Theory of Emulsions and their Technical Treatment. By WILLIAM CLAYTON. (London: J. & A. Churchill (1935). Pp. 458. 25.5 cms. × 16 cms. Price 25s.)

The first edition of Clayton's book appeared in 1923, and contained 160 pages; this third edition has nearly trebled its size. The book has developed from an excellent introduction concerning our knowledge of emulsions into an even better text-book of this subject. The very large technical literature on emulsions has been incorporated, and one finds an equally thorough treatment of emulsifiers, colloid mills, homogenisers and the manifold devices used for de-emulsification, on the one hand, and of inversion of emulsions, multiple emulsions, Mudd's interface technique, etc., on the other. Emulsions are complex systems, and any one-sided theory of their stability which excludes all others is unlikely to be the true one. Clayton is therefore perhaps right in discussing the possible explanations so impartially that one often does not know which of them he considers the most probable.

H. F.

TWO INORGANIC COMPLEXES HAVING IN SOLUTION AN EXCEPTIONALLY HIGH VERDET CONSTANT.

BY RENÉ LUCAS AND FERNAND GALLAIS.

Received 16th April, 1936.

As long ago as 1886 Cornu and Potier,¹ studying the influence of the angle of the magnetic field and of the luminous ray on magnetic rotation, made use of "Thoulet liquor" which has a magnetic rotatory power three times greater than that of carbon bisulphide. Several subsequent measurements have confirmed the exceptional position of this solution and it always holds first place amongst the liquids having a high Verdet constant.^{2, 3}

One of us having utilised this property for determining the chemical constitution of dilute solutions of alkali iodomercurates,⁴ we have resumed the study of such solutions. We have shown that their main constituent, a salt of H_2HgI_4 has an exceptional specific magnetic rotatory power and dispersion, which we have sought to interpret on the grounds of luminous absorption.⁵ We were led, later, to investigate the analogous properties of solutions of alkali iodobismuthates.

Recent work having involved the preparation of saturated solutions of complex salts, both of iodomercurates and iodobismuthates of potassium, we hoped to obtain liquids having an exceptionally high magnetic rotatory power. These are the subject of the present communication.

1. Preparation of Solutions.

The two solutions in question were adopted after several investigations of other less favourable ones; their composition was thus chosen so that they would have a maximum content of complex salts.

Saturated Potassium Iodomercurate Solution.—Pernot⁶ determined the solubility isotherms of the system $HgI_2 + KI$ in water at different temperatures. The proportions of the two iodides used are approximately those of a saturated solution of HgI_2 , KI , H_2O at 20° C. and, indeed, our solution contains some characteristic crystals of this complex, although it goes without saying that these crystals may differ from the complex anions existing in solution.

Composition: KI 9.25 gm. *Density:* d_4^{19} 3.16.
 HgI_2 12.75 gm.
 H_2O 3.00 gm.

¹ A. Cornu and A. Potier, *Comptes rend.*, 1886, 102, 385.

² O. Schönrock, *Z. physik. Chem.*, 1893, 11, 782.

³ L. R. Ingersoll, *J. Opt. Soc. Am.*, 1922, 6, 663.

⁴ F. Gallais, *Comptes rend.*, 1935, 200, 836; 1936, 202, 54.

⁵ R. Lucas and F. Gallais, *Comptes rend.*, 1936, 202, 129.

⁶ Mlle. M. Pernot, *ibid.*, 1927, 185, 950.

Saturated Solution of Potassium Iodobismuthates.—Delwaulle⁷ worked out the solubility isotherms of the system $\text{BiI}_3 + \text{KI}$ in water. The proportions of the two iodides used are approximately those of a saturated solution of the two salts BiI_3 , KI , H_2O and BiI_3 , 2KI , H_2O ; this will deposit one or other of these salts as the proportion of alkali iodide is slightly diminished or increased. We extrapolated for the temperature 25° the curves given for 15° and 35° . At the temperature of 20° at which we worked a fair number of crystals were deposited from the solution.

Composition : KI 5.0 gm.
 BiI_3 5.90 gm.
 H_2O 2.60 gm.
 HCl one drop.

Density : d_4^{10} 2.54.

The preparation of the two solutions presents no difficulty; the iodides dissolve readily together in both cases on slightly warming the mixture of the three constituents.

2. Experimental.

We used for our measurements light from a mercury or cadmium arc of wave-length λ 0.6438 μ , 0.5780 μ , 0.5461 μ and 0.4662 μ . The two solutions being highly coloured (yellow for mercuriiodides and red for bismuthiiodides) and absorbing considerably in the blue and green respectively, we examined them in thicknesses of 5 or even 1.07 mm. The two vessels were placed between the poles of an electromagnet which, with a current of 14 amps. had a magnetic field of about 14,600 gauss per cm. The analyser permitted accurate measurement to one-hundredth of a degree; but, if the double rotation observed for the solutions varied from 19 to 51° , the results obtained with water are much less pronounced— 3.33° for a thickness of 5 mm., and 0.79° for 1.07 mm. so that, specially in the latter case, the Verdet constants are only known to within 2 or 3 per cent. in relative values. The results are shown in Table I. It will be seen that by using

TABLE I.

Wavelength (in μ).	Double Rotation, Observed for a Magneto-Optical Field of		Verdet Constant at 20° .	
	1546 gauss/cm. (1.07 mm.).	7345.5 gauss/cm. (5 mm.).	Observed.	Related to that of Water.
A. Potassium Iodobismuthates.				
0.6438 (red)	—	51.28°	0.209	—
0.5780 (yellow)	19.89°	—	0.386	28.3
B. Potassium Iodomercurate.				
0.6438 (red)	—	27.37°	0.112	—
0.5780 (yellow)	—	38.14°	0.156	11.4
0.5461 (green)	—	46.20°	0.189	12.3
0.4662 (blue)	19.15°	—	0.370	17.7

the iodobismuthate solution from red to yellow and iodomercurate from yellow to blue one can obtain magnetic rotations from 18 to 28 times greater than those of water.

⁷ Mlle. M. L. Delwaulle, *Comptes rend.*, 1934, 199, 948.

Summary.

1. Having studied the exceptional magnetic rotatory power of solutions of iodomercurates we now put on record the same characteristics of iodobismuthate solutions.

2. Solutions of two complexes giving a maximum rotatory power were prepared, advantage being taken of the known solubility isotherms of the systems $\text{HgI}_2 + \text{KI}$ and $\text{BiI}_3 + \text{KI}$ in water.

3. Saturated solutions were thus obtained of complex salts having a specific rotatory power 18 to 28 times greater than that of water.

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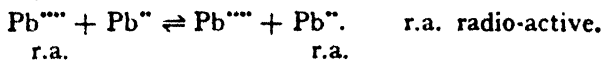
OXIDATION-REDUCTION POTENTIALS IN NON-AQUEOUS SOLUTIONS. PART II.

BY J. R. PARTINGTON AND J. W. SKEEN.

Received 2nd April, 1936.

The present communication is an extension of the work described in Part I.¹ to other systems and to other solvents such as acetonitrile, benzonitrile and acetone. These solvents and pyridine are of interest from the point of view of the mechanism of the formation of a potential at an oxidation-reduction electrode since they do not ionise to give hydrogen or hydroxide ions.

One series of measurements has been made in anhydrous acetic acid and although this solvent ionises to give hydrogen ions, the results are nevertheless interesting on account of the investigations of von Hevesy and Zechmeister.² They found from measurements with lead acetate and lead tetra-acetate in acetic acid with the help of a radio-active indicator that an electrolytic oxidation can take place through a direct transfer of charge. Equimolecular amounts of radio-active plumbic acetate and ordinary plumbous acetate (or *vice versa*) were dissolved in acetic acid followed by separation of the two lead salts after a short time. A uniform distribution of lead isotopes between the plumbic and plumbous compounds was found to occur between the molecules and it was concluded that a dynamic equilibrium was set up between the plumbic and plumbous ions according to the scheme :



If an electrode is present in the system it could participate in the transfer of charges. These authors point out, however, that this is not the only mechanism possible, and that electrolytic oxidations or reductions may take place in some cases through the participation of the solvent.

Experimental.

Preparation of Materials.—(See also Part I.)

Cupric Bromide was prepared by treating A.R. copper with a slight excess of A.R. bromine in the presence of a little water, as recommended

¹ Partington and Skeen, *Trans. Faraday Soc.*, 1934, **30**, 1062.

² Von Hevesy and Zechmeister, *Z. Elektrochem.*, 1920, **26**, 151.

by Richards.³ It was kept in a vacuum desiccator over phosphorus pentoxide.

Cuprous Bromide.—A warm dilute solution of cupric bromide, prepared as above, was reduced by sulphur dioxide. The cuprous bromide was kept in the dark in a vacuum desiccator over phosphorus pentoxide.

Cupric Thiocyanate was obtained by taking a moderately concentrated air-free solution of A.R. potassium thiocyanate acidified with a little sulphuric acid and adding immediately the calculated quantity of a concentrated air-free solution of A.R. copper sulphate. The black precipitate was quickly filtered off, washed with a little air-free water, pressed between filter papers and dried in a desiccator over sulphuric acid.

Cuprous Thiocyanate was prepared by reducing a solution containing the appropriate amounts of copper sulphate and potassium thiocyanate with sulphur dioxide.

Lead Tetra-acetate prepared by adding red lead slowly to a mixture of acetic acid and acetic anhydride at 55°-65°, was recrystallised from a mixture of the acid and anhydride, washed with cold acetic acid and dried in a desiccator over sulphuric acid.

Anhydrous Lead Acetate.—A.R. lead acetate was recrystallised three times from conductivity water containing a little acetic acid. The crystals were dehydrated by leaving in a vacuum desiccator over phosphorus pentoxide.

Lithium Acetate.—Pure lithium carbonate was treated with a slight excess of dilute (1 : 1) acetic acid. The solution when evaporated set to a jelly which crystallised overnight. It was recrystallised twice from redistilled 96 per cent. alcohol, dried at 100°, and kept in a vacuum desiccator over phosphorus pentoxide.

Purification of Solvents.

Pyridine.—In the purification described in Part I., it is advisable to reflux the pyridine with a small quantity of potassium permanganate after the initial fractionation. The pyridine was then distilled and the refluxing with barium oxide followed as usual.⁴ Commercial barium oxide was suitable if the following procedure was adopted. After the initial fractionation the pyridine was refluxed for six hours with a mixture of barium oxide and potassium permanganate. After distillation it was refluxed with a fresh quantity of barium oxide. It was then finally fractionated from a little barium oxide in an atmosphere of dry nitrogen.

The procedure of keeping and using the solvents described in Part I. was adopted. As the solvents were to be used for solutions of substances such as ferrous chloride and cuprous chloride which are easily oxidised, air was prevented from dissolving in the pure solvent and the last fractionation was done in an atmosphere of dry nitrogen.

Acetonitrile was purified by shaking with half its volume of water and then adding solid potassium carbonate until no more dissolved; after separating, the acetonitrile was allowed to stand over a little solid caustic potash for a day, then decanted and allowed to stand over calcium chloride for a week. After distillation it was allowed to stand over a little phosphorus pentoxide for a day. If the first lot of phosphorus pentoxide liquefied it was replaced by some fresh pentoxide until it remained as a lumpy white powder. The liquid was then fractionated in an atmosphere of dry nitrogen with a 12-pear column using the usual precautions to keep out moisture. After standing over some fresh phosphorus pentoxide it was again fractionated in an atmosphere of dry nitrogen and the fraction boiling at 81.5° C. at 760 mm. was collected in the stock bottle. The density found

³ Richards, *Proc. Amer. Acad.*, 1890, **25**, 206; *Chem. News*, 1891, **63**, 20.

⁴ Mathews and Johnson, *J. Physical Chem.*, 1917, **21**, 294.

was $\Delta_4^{25^\circ} = 0.7767 \pm 0.0001$. The International Critical Tables (Vol. III., p. 28) give $\Delta_4^{25^\circ} = 0.7770$.⁵

Benzonitrile was steam distilled and the distillate extracted with ether. The ethereal layer was washed with dilute caustic soda solution and then with dilute sulphuric acid. The product was then allowed to stand over calcium chloride for a few days. After removing the ether on a water-bath it was fractionated under reduced pressure (b.-pt. 120° C. at 10 cm.) using a 25 cm. Hempel column. The middle fraction was left for a day over a little phosphorus pentoxide and then again fractionated under reduced pressure from a little fresh pentoxide. Nitrogen was used to fill the apparatus and also when the pressure was raised. The density found was $\Delta_4^{25^\circ} = 1.0008 \pm 0.0001$. The value given in the International Critical Tables (Vol. III., p. 28) is $\Delta_4^{25^\circ} = 1.0005 \pm 0.0003$.

Acetone was dried by means of anhydrous potassium carbonate.^{6, 7, 8, 9} Acetone (Griffin and Tatlock's A.K.) was allowed to stand over potassium permanganate for 24 hours with occasional shaking. After distillation it was left for a few days with occasional shaking over anhydrous potassium carbonate previously dehydrated at 200° – 300° C. for several hours. The acetone was then fractionated using a 75 cm. Hempel column in dry nitrogen, being protected from the atmosphere by calcium chloride and soda-lime tubes. This fractionation from potassium carbonate was carried out two more times, a good deal of the first and last fractions being neglected. The acetone used boiled at 56.3° C. at 760 mm. and had a density of $\Delta_4^{25^\circ} = 0.7847 \pm 0.0001$. Lannung⁸ gives $\Delta_4^{18^\circ} = 0.7921$; $\Delta_4^{37^\circ} = 0.7702$, which give by interpolation $\Delta_4^{25^\circ} = 0.7841$. The interpolated value for 20° , namely, $\Delta_4^{20^\circ} = 0.7898$ agrees fairly well with the value of Bell and co-workers⁶ and Price¹⁰ who give 0.7908 . The refractive index for sodium light was found to be 1.35715 at 25° C.

Acetic Acid was dehydrated by triacetyl borate.¹¹ Triacetyl borate is an excellent dehydrating agent since it reacts with water to yield acetic acid and insoluble boric acid: it was prepared according to the directions of Pictet and Geleznoff.¹²

A.R. acetic acid (Griffin and Tatlock) was refluxed with the triacetyl borate and then carefully fractionally distilled using a Hempel column: 2 of 4 times the amount calculated to react with the water present was used. The fraction boiling at 117.0° C. (760 mm.) was collected. Bousfield and Lowry¹³ give the boiling-point as 117.88° C. $\pm 0.05^\circ$ at 760 mm. and the freezing-point as 16.60° C. $\pm 0.005^\circ$. Eichelberger and La Mer give the freezing-point as 16.60° C. $\pm 0.01^\circ$. The freezing-point of the product used was 16.59° C. $\pm 0.01^\circ$.

Apparatus and Procedure.

To prevent risk of contamination of the solutions by water, in most cases a reference electrode was used in which the solvent was the same as on the other side of the cell. Thus the reference electrode, $\text{Ag} | \text{AgCl}$ in pyridine, was used in the case of pyridine solutions. In two cases (solutions in benzonitrile and acetone) suitable reference electrode solutions which could be kept for about 3 or 4 weeks could not be found.

⁵ Timmermans, *Sci. Proc. Roy. Dublin Soc.*, 1912, **13**, 310; and others.

⁶ Bell and co-workers, *J. Chem. Soc.*, 1930, 1927.

⁷ Walden and Birr, *Z. physikal. Chem.*, 1931, **153**, 1.

⁸ Lannung, *ibid.*, 1932, **161**, 255, 269.

⁹ Birr, *ibid.*, 1933, **165**, 311.

¹⁰ Price, *J. Chem. Soc.*, 1919, **115**, 1116.

¹¹ Eichelberger and La Mer, *J. Amer. Chem. Soc.*, 1933, **55**, 3633.

¹² Pictet and Geleznoff, *Ber.*, 1903, **36**, 2219.

¹³ Bousfield and Lowry, *J. Chem. Soc.*, 1911, **99**, 1432.

Here it was necessary to refer the potentials to aqueous solutions and the non-aqueous solutions and the aqueous potassium chloride bridge solution were separated by a ground glass-plug to prevent diffusion. Risk of contamination of the non-aqueous solution by water near the electrode was slight, the taps being kept closed except during actual measurements (Fig. 3, Cell IIa).

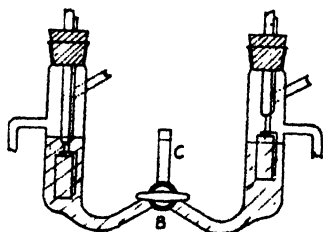


FIG. 1.—Cell Ia.

In measurements using acetic acid as solvent, the potentials were referred to the aqueous calomel electrode by a method similar to that described by Conant and co-workers,¹⁴ a saturated solution of lithium acetate in acetic acid being used as bridge solution to separate the aqueous and non-aqueous electrode solutions (Fig. 4, Cell III).

A modification of the cell previously described was used for the pyridine solutions. In this, the connecting tap was reversed (Cell Ia, Fig. 1) in order to facilitate the levelling of the solutions.

In certain cases (where the solvent was acetonitrile) the conductivity of the solutions was good and the two electrode solutions could be separated by a ground-glass plug to prevent diffusion (Cell II, Fig. 2).

All solutions were made up by weight in an atmosphere of dry nitrogen as previously described.

As the solutions used, however, were so dilute that the density did not differ much from that of the pure solvent, the error involved in using the latter figure to calculate the volume of the solution was much less than other experimental errors. The value of the concentration was only necessary in order that a check could be kept on the total concentration of the salts used.

Preparation of the Electrodes.—In a few cells gold as well as platinum electrodes were used. Pieces of gold foil approximately 2 cm. by 1 cm. were suspended by being fused on gold wire. This was fused to platinum wire sealed into glass tubing. Connection was made by silver wire fused to the platinum.

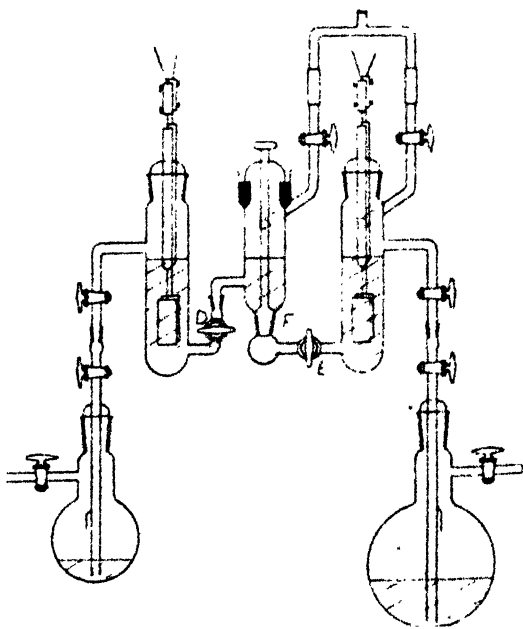


FIG. 2.—Cell II.

The 0.1N-calomel electrode¹⁵ had a three-way stopcock to enable fresh calomel electrode solution to be run in through the side-arm in place of

¹⁴ Hall and Conant, *J. Amer. Chem. Soc.*, 1927, 49, 3047; Conant and Werner, *ibid.*, 1930, 52, 4436.

¹⁵ Lewis, Brighton and Sebastian, *ibid.*, 1917, 39, 2245.

two separate stopcocks. The mercurous chloride was made electrolytically. The cells were first filled with dry nitrogen.

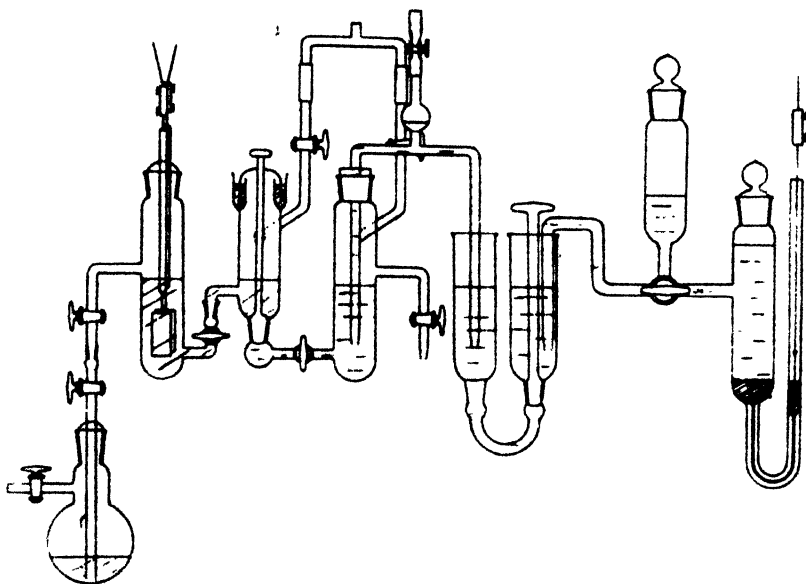


FIG. 3.—Cell IIa.

Cell Ia.—After connecting the right-hand limb and the outlet tube (C) by means of the tap B, the solution was forced over into the right-hand compartment to the level marked on the outlet tube. The tap was then turned round a little way and the small amount of liquid in C was removed by a roll of filter paper. A slight pressure was then established in the left-hand limb by commencing to force over the other solution. On turning the tap B so as to connect this limb and the outlet tube, the small amount of liquid in the bore of the tap was blown into C and was then removed by filter paper. The left-hand limb was then filled to the same level as the mark on C. The excess liquid in C was then removed by a roll of filter paper. The mark on C was so arranged that by this means the correct amount of solution was run into the electrode vessels.

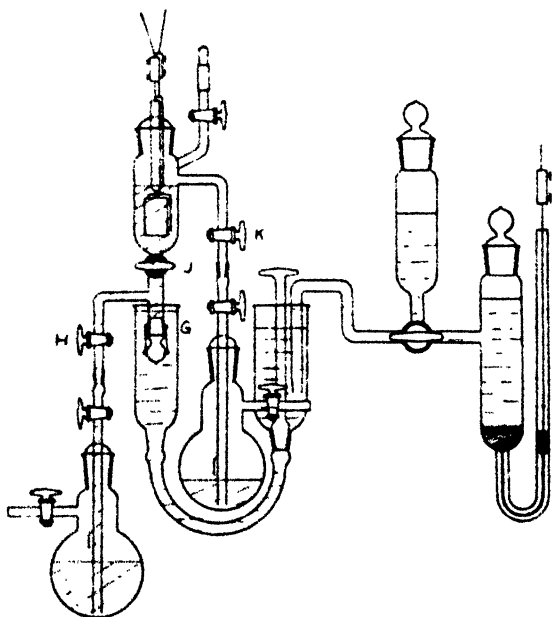


FIG. 4.—Cell III.

Cell II.—The right-hand limb as far as the ground-glass plug (F) was first filled by manipulation of the tap E. The left-hand limb and the middle compartment were filled afterwards. Taps D and E were kept closed except during measurements.

Cell IIa.—Saturated potassium chloride solution was put in the right-hand limb as far as the ground-glass plug and filling continued as described above. The intermediate apparatus between the actual cell and the calomel electrode was used to separate the saturated and 0.1N potassium chloride solutions.

Cell III.—The ground-glass stopper (G) was placed tightly in position and the saturated potassium chloride solution placed in the intermediate vessel. The solution rose just to the top of the stopper. The non-aqueous bridge solution was then run in through the tap H till it just filled the bore of the tap J. The electrode solution was then run in through the tap K. The tap J was opened only while measurements were being made.

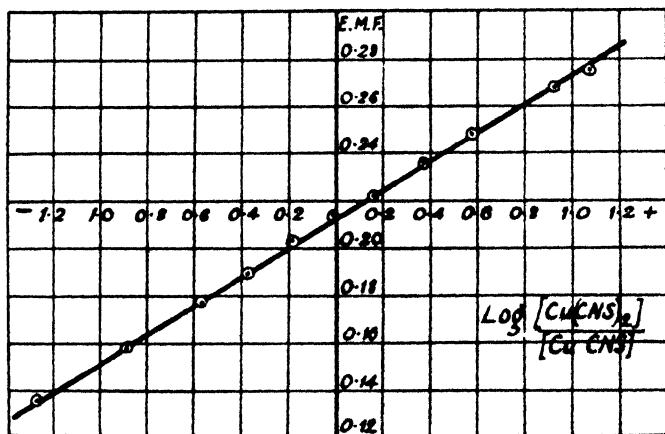
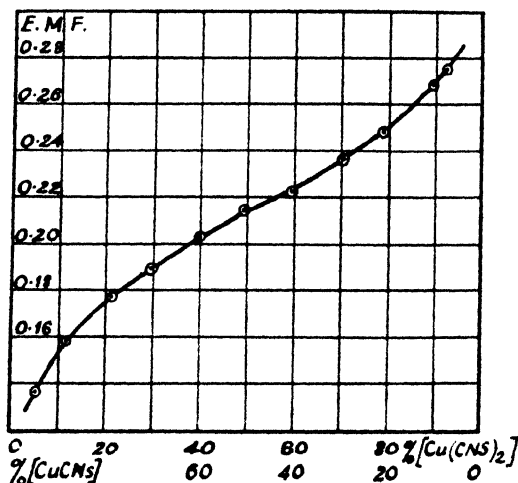


FIG. 5.—Series IV.

Limits of Accuracy.—Readings were taken to the nearest millivolt in all cases except the systems cupric-cuprous chlorides and cupric-cuprous bromides in acetonitrile where they could easily be measured to a tenth of a millivolt, even when using

the cell with the ground-glass plug. Actually, the latter system was seldom measured to less than a millivolt, as the potentials varied rapidly. The electromotive forces were measured at 25° C., the cell being in an air thermostat.

Results.

Series IV.—Cell Ia used (Table I., Fig. 5). Equilibrium was established almost immediately and the electromotive force remained constant for at least an hour—for eight of the cells it remained constant for about three hours. It then slowly decreased.

TABLE I.

+ Pt		Cu(CNS) ₂ in pyridine.		AgCl in pyridine (0.0244 M.)		Ag—.	
		CuCNS					
Conc. CuCNS. (Molar).	Conc. Cu(CNS) ₂ (Molar).	Total Conc. (about 0.023 M.).	Ratio $\frac{[\text{Cu(CNS)}_2]}{[\text{CuCNS}]}$.	Log $\frac{[\text{Cu(CNS)}_2]}{[\text{CuCNS}]}$.	Per Cent. $[\text{Cu(CNS)}_2]$.	E.M.F. (Volt).	
0.02053	0.00108	0.02161	0.0524	-1.281	5.0	0.136	
0.02117	0.00274	0.02391	0.1292	-0.8887	11.4	0.158	
0.01886	0.00502	0.02388	0.2662	-0.5748	21.0	0.177	
0.01568	0.00654	0.02222	0.4176	-0.3792	29.5	0.189	
0.01359	0.00883	0.02242	0.6503	-0.1869	39.4	0.203	
0.01213	0.01172	0.02385	0.9659	-0.0151	49.1	0.214	
0.01000	0.01438	0.02438	1.440	0.1584	59.0	0.222	
0.00655	0.01541	0.02196	2.355	0.3720	70.2	0.236	
0.00489	0.01815	0.02304	3.713	0.5698	78.8	0.248	
0.00265	0.02202	0.02467	8.302	0.9192	89.2	0.268	
0.00205	0.02386	0.02591	11.66	1.067	92.1	0.275	

A solution of cupric bromide in pyridine decomposes and the system $\text{CuBr}_2/\text{CuBr}$ could not be measured.

Series V.—Cell II used (Table II., Fig. 6). An oxidation-reduction system itself was used as a reference electrode (shown on the right) and the solution was stable throughout the whole series of measurements. Equilibrium was established almost immediately; the E.M.F., after remaining constant to within a tenth of a millivolt for about an hour, slowly decreased; it remained constant to within a millivolt for more than 5-6 hours. In the cells in which the

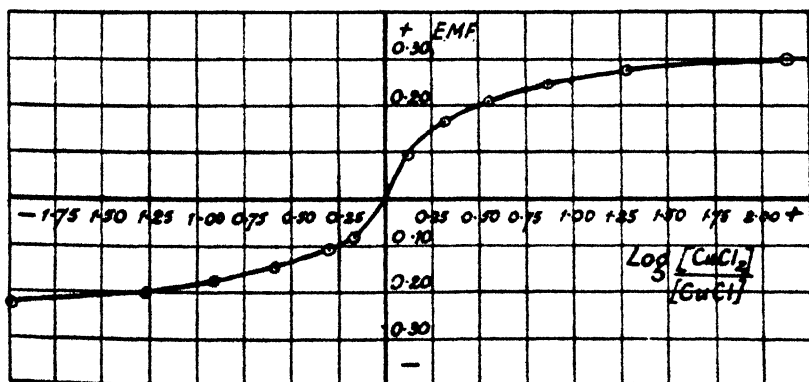
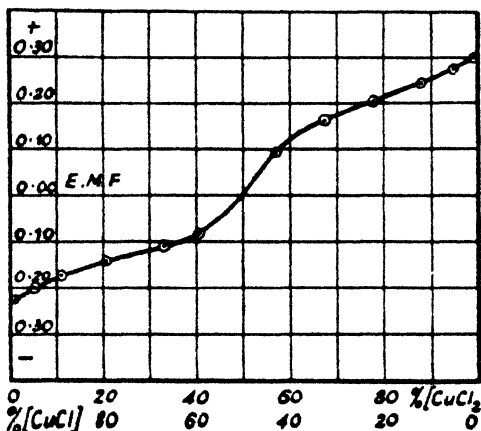


FIG. 6.—Series V.

concentration of cupric chloride was over 90 per cent., however, the E.M.F. fell continuously.

TABLE II.

Pt $\left \begin{array}{l} \text{CuCl}_2 \\ \text{CuCl} \end{array} \right $ in acetonitrile.		CuCl_2 (0.03245 M.) CuCl (0.03237 M.) in acetonitrile.		Pt.		
Conc. CuCl (Molar).	Conc. CuCl ₂ (Molar).	Total Conc. (about 0.04 M.).	Ratio $\frac{[\text{CuCl}_2]}{[\text{CuCl}]}$.	Log $\frac{[\text{CuCl}_2]}{[\text{CuCl}]}$.	Per Cent. [CuCl ₂].	E.M.F. (volt.).
0.04162	0.00043	0.04205	0.0102	-1.989	1.0	-0.2285
0.03944	0.00212	0.04156	0.0537	-1.270	5.1	-0.2000
0.04319	0.00527	0.04846	0.1220	-0.9137	10.9	-0.1740
0.03391	0.00868	0.04259	0.2560	-0.5919	20.4	-0.1435
0.03196	0.01581	0.04777	0.4947	-0.3057	33.1	-0.1090
0.02639	0.01786	0.04425	0.6766	-0.1697	40.4	-0.0819
0.02021	0.02662	0.04683	1.318	0.1198	56.9	0.0921
0.01409	0.02928	0.04337	2.077	0.3175	67.5	0.1631
0.00808	0.02853	0.03661	3.531	0.5479	77.9	0.2056
0.00410	0.03016	0.03426	7.351	0.8664	88.0	0.2445
0.00167	0.03198	0.03365	19.16	1.282	95.0	0.2752
0.00017	0.02286	0.02303	133.9	2.127	99.3	0.2995

The effect of dilution on a solution in which the concentration ratio was kept constant was measured.

+ Pt $\left \begin{array}{l} \text{Stock Solution.} \\ \text{Total Concentration} \\ = 0.06482 \text{ M.} \end{array} \right $		$\left \begin{array}{l} \text{Diluted Stock Solution.} \\ \text{Total Concentration} \\ = 0.04548 \text{ M.} \end{array} \right $		Pt -.
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E.M.F. = 2.7 millivolts.

Further dilution to about 0.022 M. increased the potential to 6.5 millivolts. Thus, the effect produced on the electromotive forces of the cells measured by not using solutions of exactly the same total concentration throughout was negligible when compared with differences of potential produced by variation of the concentration ratio.

In a few preliminary measurements an attempt was made to use the reference electrode copper/copper chloride in acetonitrile as in the case of pyridine (Series I). This was discontinued as the green solution of cupric chloride in acetonitrile turned brown in about half an hour in contact with a copper electrode which was also blackened just as in the case of the measurements with pyridine.

Series VI. Cell II used.

+ Pt $\left \begin{array}{l} \text{CuBr}_2 \\ \text{CuBr} \end{array} \right $ in acetonitrile.		$\left \begin{array}{l} \text{CuBr}_2 (0.02427 \text{ M.}) \\ \text{CuBr} (0.02426 \text{ M.}) \end{array} \right $ in acetonitrile.		Pt -.
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Reference Electrode.

The results obtained were in all cases smaller than the theoretical E.M.F. but were usually approximately constant for about three hours.

Measurements of this series were also made with the reference electrode

Pt $\left \begin{array}{l} \text{CuCl}_2 \\ \text{CuCl} \end{array} \right $ in acetonitrile which was used in the previous series and found to be stable.	
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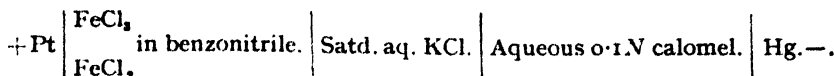
Series VII. Cell II used.

+ Pt $\left \begin{array}{l} \text{CuBr}_2 \\ \text{CuBr} \end{array} \right $ in acetonitrile.		$\left \begin{array}{l} \text{CuCl}_2 (0.02322 \text{ M.}) \\ \text{CuCl} (0.02285 \text{ M.}) \end{array} \right $ in acetonitrile.		Pt -.
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Reference Electrode.

Measurements were made with both platinum and gold electrodes but the potentials were not steady. The potential with the gold electrode was initially 0.05 volt more negative than that with the platinum, but this difference fell to 3 to 10 millivolts after about three hours. Addition of a little cupric chloride as a potential mediator had no effect. Changes of colour in the solutions in all cases indicated decomposition.

Series VIII. Cell IIa used.



Difficulty was experienced in getting the ferrous chloride to dissolve. Owing to this, and also to the fact that extremely dilute solutions had to be used, the values obtained were probably not equilibrium values, although in nearly every case the potential remained constant for about an hour.

The solubility of cupric chloride appeared to be too small to allow measurement of the system $\text{CuCl}_2/\text{CuCl}$ to be made.

Although both ferric and ferrous chlorides are soluble in acetonitrile no measurements could be made with this pair of salts as a solution of the two decomposed within an hour.

Series IX. Cell IIa used (Table III., Fig. 7). Although the solutions were made up just before the cell was filled

they gradually decomposed during the measurement, so that the values given can be regarded as approximate only. Reference electrodes using acetone as solvent:

c.g. Ag/AgCl (s), saturated LiCl in acetone,
and $\text{Hg}/\text{Hg}_2\text{Cl}_2$ (s), saturated LiCl in acetone.

were not used, since (1) solutions of ferric chloride and lithium chloride in acetone react to give an orange precipitate; (2) mercurous chloride in

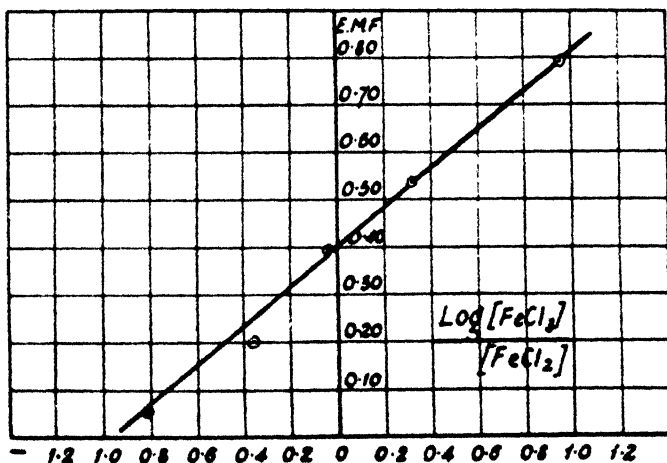
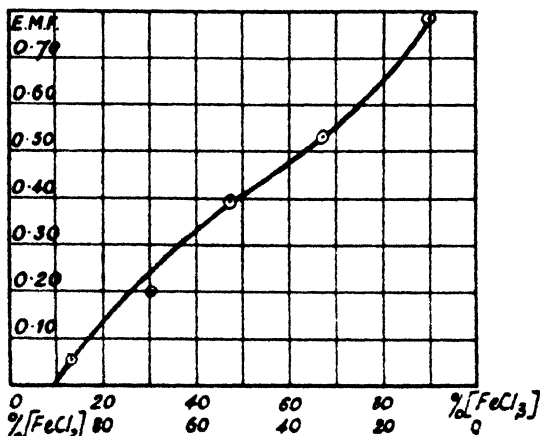


FIG. 7.—Series IX.

TABLE III.

+ Pt	FeCl ₃ in acetone. FeCl ₃	Satd. aq. KCl.	Aqueous 0.1 N calomel.	Hg—.		
Conc. FeCl ₃ (Molar).	Conc. FeCl ₃ (Molar).	Total Conc. (about 0.04 M.).	Ratio [FeCl ₃] [FeCl ₂].	Log [FeCl ₃] [FeCl ₂].	Per Cent. [FeCl ₃].	E.M.F. (volt).
0.03246	0.00493	0.03739	0.1519	—0.8185	13.2	0.055
0.03067	0.01320	0.04387	0.4302	—0.3664	30.1	0.200
0.02256	0.02032	0.04288	0.9008	—0.0454	47.4	0.392
0.01494	0.03096	0.04590	2.073	0.3167	67.5	0.533
0.00402	0.03628	0.04030	9.021	0.9552	90.0	0.788

a solution of lithium chloride in acetone reacts to give a grey product ;
(3) the process of solution in non-aqueous solutions is sometimes slow and

so saturation might not always be obtained if fresh solutions were to be made up for each cell.

Series X. Cell III used (Table IV., Fig. 8). The potentials with the platinum electrodes were not very definite: the potential increased rapidly for about one to two hours to the value given, then remained constant for about half an hour, and afterwards slowly increased. The potential at the gold electrode re-

mained practically constant for about two to three hours after only a small increase.

Some platinum electrodes gave unreliable results. New platinum foil gave results similar to old pieces which had been used several times.

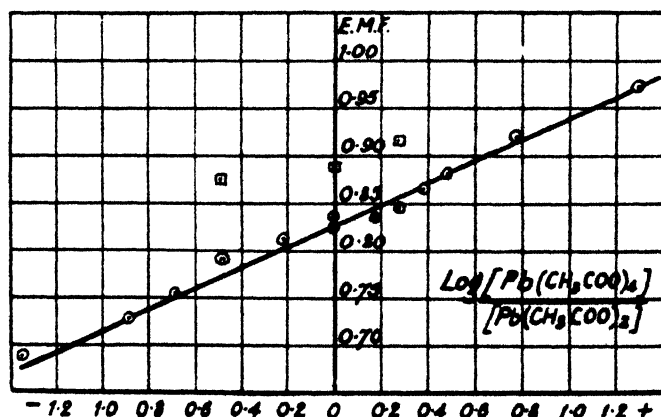
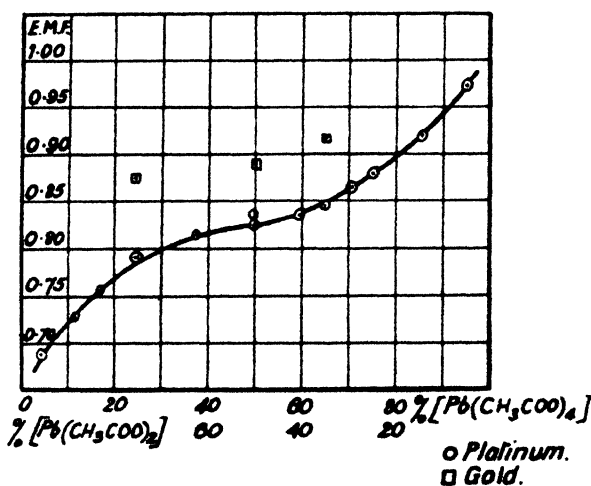


FIG. 8.—Series X.

Electrodes washed in alcohol and heated in a flame nearly always gave

TABLE IV.

+ Pt + Au	$\text{Pb}(\text{CH}_3\text{COO})_2$ $\text{Pb}(\text{CH}_3\text{COO})_2$	in acetic acid.	Saturated CH_3COOLi in acetic acid.	Satd. aq. KCl.	Aqueous 0.1 N calomel.	Hg—.
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Conc. $\text{Pb}(\text{CH}_3\text{COO})_2$ (Molar).	Conc. $\text{Pb}(\text{CH}_3\text{COO})_2$ (Molar).	Total Conc. (about 0.04 M.).	Ratio $\frac{[\text{Pb}(\text{CH}_3\text{COO})_2]}{[\text{Pb}(\text{CH}_3\text{COO})_2]}$	Log $\frac{[\text{Pb}(\text{CH}_3\text{COO})_2]}{[\text{Pb}(\text{CH}_3\text{COO})_2]}$	Per Cent. $\frac{[\text{Pb}(\text{CH}_3\text{COO})_2]}{[\text{Pb}(\text{CH}_3\text{COO})_2]}$	E.M.F. (Platinum).	E.M.F. (Gold).
0.03713	0.00167	0.03880	0.0449	-1.3477	4.3	0.688	—
0.03183	0.00413	0.03596	0.1299	-0.8863	11.5	0.727	—
0.03091	0.00624	0.03720	0.2035	-0.6915	16.9	0.755	—
0.02638	0.00853	0.03491	0.3233	-0.4904	24.4	0.790	0.874
0.02861	0.00949	0.03810	0.3318	-0.4792	24.9	0.790	—
0.02458	0.01473	0.03931	0.5991	-0.2225	37.5	0.813	—
0.01838	0.01824	0.03662	0.9920	-0.0035	49.8	0.835	—
0.01808	0.01797	0.03605	0.9942	-0.0025	49.9	0.825	0.888
0.01471	0.02171	0.03642	1.476	0.1692	59.6	0.835	—
0.01164	0.02165	0.03329	1.860	0.2696	65.0	0.845	0.916
0.01132	0.02607	0.03829	2.383	0.3772	70.4	0.865	—
0.00879	0.02645	0.03523	3.010	0.4786	75.1	0.880	—
0.00546	0.03207	0.03753	5.868	0.7685	85.4	0.920	—
0.00180	0.03495	0.03675	19.40	1.2877	95.1	0.973	—

indefinite results. The gold electrode was least affected by washing with alcohol and heating in a flame.

In order to compare some of the results with those of Abegg and Neustadt,¹⁸ in two other cases, namely, the systems $\text{CuCl}_2/\text{CuCl}$ in acetonitrile and $\text{Cu}(\text{CNS})_2/\text{CuCNS}$ in pyridine, the potentials were referred to aqueous solutions using the same method as employed in series VIII. and IX. (Cell IIa). The first cell measured was ($[\text{CuCl}_2]/[\text{CuCl}] = 1$):

+ Pt	CuCl_2 CuCl	in acetonitrile.	Satd. aq. KCl.	Aqueous 0.1N. calomel.	Hg—.
e_1			e_2		e_3

$$E = e_1 - e_2 + e_3 = 0.565 \text{ volt.}$$

Taking $e_3 = 0.333$ (value for 0.1N calomel at 25° C., the liquid junction potential between the saturated and 0.1N potassium chloride solutions being negligibly small) and neglecting the liquid junction potential between the aqueous and non-aqueous solutions, we find:

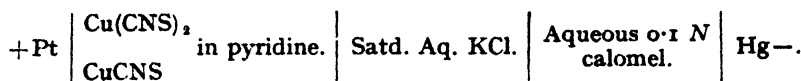
$$e_1 = E_0 + \frac{RT}{F} \log_e \frac{[\text{CuCl}_2]}{[\text{CuCl}]} = 0.898.$$

$$\therefore E_0 = 0.898, \text{ since } \log \frac{[\text{CuCl}_2]}{[\text{CuCl}]} = 0.$$

This is the value of the normal oxidation-reduction potential of the system $\text{CuCl}_2/\text{CuCl}$ in acetonitrile if we assume the liquid junction potential is negligible and the ratio of the activities of the cupric and cuprous ions is equal to the ratio of the concentrations of the salts.

¹⁸ Abegg and Neustadt, *Z. Elektrochem.*, 1909, **15**, 264.

The other cell measured ($[\text{Cu}(\text{CNS})_2]/[\text{CuCNS}] = 1$) was :



$$E = e_1 - e_2 + e_3 = 0.050.$$

Whence

$$E_0 = 0.383.$$

This is close to Abegg and Neustadt's value of 0.37 volt for the system $\text{CuCl}_2/\text{CuCl}$ in pyridine, although the agreement is fortuitous. Thus, the value of E_0 for the system $\text{CuCl}_2/\text{CuCl}$ in pyridine, although it has not been measured in the present research, is on the assumptions made above about 0.28 volt, about 0.10 volt less than that of the $\text{Cu}(\text{CNS})_2/\text{CuCNS}$ system. The reference electrodes in the two series were nearly the same and the electromotive forces of the former were found to be about 0.10 volt less than those of the second system. These various values differ considerably from the value of E_0 for aqueous solutions, namely 0.16 volt.

Abegg and Neustadt's conclusion that the normal oxidation-reduction potential was the same in pyridine as in water does not seem to be correct. Some of the difference may be accounted for by the different degrees of dissociation of the salts in the non-aqueous solutions and also by some error probably made in neglecting the liquid junction potential.

The following approximate solubilities at 25° C. were determined to complete the data on the solubilities of the salts employed.

Pyridine. Cupric thiocyanate, 0.045*M*. Cuprous thiocyanate contains more than 20 gms. per litre.

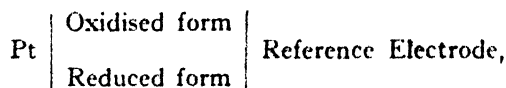
Benzonitrile. Anhydrous ferrous chloride, 0.012*M*.

Acetone. Anhydrous ferrous chloride, 0.147*M*. Potassium ferricyanide is insoluble.¹⁷

Acetic acid. Lead tetra-acetate, 0.075*M*. Anhydrous lead acetate, 2.03*M*. Lithium acetate approximately 1.83*M*.

Discussion.

The electromotive force of the cell :



can be expressed by the equation (Peters' formula) :

$$E = E_0' + \frac{RT}{nF} \log_e \frac{[\text{Oxidised form}]}{[\text{Reduced form}]}$$

E_0' is a constant which includes the potential of the reference electrode, the liquid junction potential (assumed to remain constant), and the normal oxidation-reduction potential of the system. On the assumption that the ratio of the activities of the ions of oxidised and reduced forms is equal to the ratio of the concentrations of oxidised and reduced salts, the logarithm of this ratio (as abscissa) plotted against E (as ordinate) should approximate to a straight line. When the potentials were definite the only exception found was the system $\text{CuCl}_2/\text{CuCl}$ in acetonitrile.

¹⁷ Cf. Naumann, *Ber.*, 1904, **37**, 4328.

E has also been plotted against the percentage concentration of the oxidised form. When due regard is had to the approximate assumptions involved in the equation, the agreement with similar curves for aqueous solutions is very good, especially in series IV, in which pyridine was the solvent. Series VIII. showed qualitative agreement with the equation, but owing to the small solubility of the ferrous chloride the lower part of the curve was not very definite. The solutions of ferric and ferrous chloride in acetone (Series IX.) were unstable but qualitative agreement with the formula is shown although the differences in the potentials obtained by varying the concentration ratio are much greater than those predicted by theory. Series X. shows good agreement with the oxidation-reduction equation.

The curves obtained with the cupric-cuprous chloride system in acetonitrile (Series V.) are peculiar. Both curves are fairly symmetrical about the point 50 per cent. $[\text{CuCl}_2]$ — 50 per cent. $[\text{CuCl}]$, and the one obtained by plotting E against the percentage concentration of cupric chloride can be considered to be made up of two separate oxidation-reduction curves, one lying between 0 — 50 per cent. $[\text{CuCl}_2]$ and the other between 50 — 100 per cent. $[\text{CuCl}_2]$. The shape of the curve seems to indicate the formation of a compound (or complex ion) from one molecule (or ion) of cupric chloride and one molecule (or ion) of cuprous chloride. A solution of cupric chloride in acetonitrile is pale green and a solution of cuprous chloride is practically colourless or very pale amber, whereas a solution of the two is brown, the colour being deepest when they are present in equimolecular proportions. This compound has been reported to be doubtfully present in various solutions.¹⁸

If this compound exists in the solutions in acetonitrile, there will be oxidation-reduction reactions between it and the simple salts. If the salt present in concentration lower than 50 per cent. combines completely with an equal number of molecules of the salt present in the higher concentration, then in such a solution there will really be the same number of molecules of complex as there were originally of salt in the lower concentration, and the excess of the other salt molecules.

Let the solution contain x per cent. of the oxidised form (CuCl_2) and $(100 - x)$ per cent. of the reduced form (CuCl). Two cases must be considered, viz. (1) $(100 - x) > x$, and (2) $x > (100 - x)$.

In case (1) the cuprous salt will be in excess. There will be $(100 - 2x)$ per cent. CuCl left, since approximately x per cent. has combined with the x per cent. of CuCl_2 to form x per cent. of complex, and there will be practically no CuCl_2 left. In case (2) practically all the $(100 - x)$ per cent. CuCl will combine with an equal amount of CuCl_2 to form approximately $(100 - x)$ per cent. of complex, and there will be $\{x - (100 - x)\} = (2x - 100)$ per cent. CuCl_2 left. If the complex ion is assumed to be Cu_3^{+++} , the charge difference as compared with Cu_2^{++} and 2Cu^+ is in each case unity ($y = 1$).

Thus, in the range 0 — 50 per cent. $[\text{CuCl}_2]$, we have an oxidation-reduction relation between the cuprous salt and the complex, the latter giving the higher valency ion, and in the range 50 — 100 per cent. $[\text{CuCl}_2]$ one between the complex and the cupric salt in which the latter now gives the higher valency ion. The normal oxidation-reduction potential of the latter system must be greater than that of the former to give the correct shape of the curve.

¹⁸ Kohlschütter, *ibid.*, 1904, 37, 1153.

$$E = E_0 + \frac{RT}{yF} \log_e \frac{[\text{Oxidised form}]}{[\text{Reduced form}]}$$

Case (1) $E' = E_0' + \frac{RT}{yF} \log_e \frac{x}{(100 - 2x)},$

or $E' = a' + b' \log \frac{x}{(100 - 2x)}$ where a and b are constants.

Case (2). $E'' = a'' + b'' \log \frac{(2x - 100)}{(100 - x)}.$

The values of a and b were found by taking two points on the curve (marked by asterisks in the table) and the equation checked with other points. The agreement is fairly good (Table V.).

TABLE V.

0 — 50 per cent. [CuCl ₂].			50 — 100 per cent. [CuCl ₂].		
$E' = -0.116 + 0.0694 \log \frac{x}{(100 - 2x)}.$			$E'' = 0.155 + 0.120 \log \frac{(2x - 100)}{(100 - x)}.$		
Per Cent.	E.M.F. (Obs.).	E.M.F. (Calcd.).	Per Cent.	E.M.F. (Obs.).	E.M.F. (Calcd.).
0	—	∞	60	0.119	0.119*
10	-0.179	-0.179*	70	0.175	0.170
20	-0.150	-0.149	75	0.192	0.191
25	-0.135	-0.137	80	0.212	0.212*
30	-0.125	-0.125*	90	0.252	0.263
40	-0.085	-0.095	100	—	∞

The results cannot be easily explained as entirely due to the effect of dilution on the dissociation of the two simple salts.

Thus, at the point 10 per cent. [CuCl₂], let α'_{10} be the degree of dissociation of the CuCl₂ of concentration c'_{10} , and α''_{90} the degree of dissociation of the CuCl of concentration c''_{90} .

Similarly at the point 90 per cent. [CuCl₂], let α'_{90} be the degree of dissociation of the CuCl₂ of concentration c'_{90} , and α''_{10} the degree of dissociation of the CuCl of concentration c''_{10} .

Then $E_{10} = -0.179 = E'_0 + \frac{RT}{F} \log_e \frac{\alpha'_{10} \cdot c'_{10}}{\alpha''_{90} \cdot c''_{90}}$

and $E_{90} = 0.252 = E'_0 + \frac{RT}{F} \log_e \frac{\alpha'_{90} \cdot c'_{90}}{\alpha''_{10} \cdot c''_{10}}$

Whence $\frac{\alpha'_{90}}{\alpha'_{10}} \bigg/ \frac{\alpha''_{10}}{\alpha''_{90}} = 2.41 \times 10^5$

Suppose on dilution from 90 per cent. to 10 per cent. ($c'_{90} - c'_{10}$) the degree of dissociation of the CuCl₂ ($\alpha'_{90} - \alpha'_{10}$) is affected to approximately the same extent as that of the CuCl ($\alpha''_{90} - \alpha''_{10}$) on dilution from 90 per cent. to 10 per cent. ($c''_{90} - c''_{10}$), then the above ratio indicates that *dilution* of the CuCl₂ and also of the CuCl approximately 9 times over similar concentration ranges would *decrease* the degree of dissociation of each by approximately 500 times.

Summary.

Peters' formula can be applied quantitatively to several oxidation-reduction systems in stable non-aqueous solutions : in a few cases unknown complex formation may occur giving potentials which do not agree directly with the equation but are definite, reproducible, and appear to follow a modified form of the equation. In certain cases indefinite potentials are given at unattackable electrodes.

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THE MECHANISM OF ELECTROLYTIC PROCESSES. PART III.—IRREVERSIBLE REDUCTIONS.

BY W. M. LESLIE AND J. A. V. BUTLER.

Received 6th March, 1936.

Irreversible electrolytic reductions have usually been regarded as secondary reactions between the depolariser and the hydrogen formed at the cathode, but a great variety of behaviour has been found in the numerous investigations which have been made, and it is evident that many of the operative factors are at present unknown. Thus, some substances are reduced only at high overvoltage cathodes and others require low overvoltage cathodes, while in some cases specific effects occur which have been regarded as due to the catalytic action of the metal on the reaction.

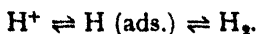
The object of the work described here was to attempt to distinguish and identify some of these factors. In general, there are three principal methods by which reduction might be effected :

- (1) by the direct transfer of electrons from the electrode to depolariser ;
- (2) by reaction between the depolariser and free (atomic) hydrogen ;
- (3) by reaction between the depolariser and adsorbed hydrogen.

In order to distinguish these cases it is necessary in the first place to know in what state hydrogen is formed at the electrode. Two distinct types of mechanism for the discharge of hydrogen ions have been proposed :

(A) The primary act is the transfer of electrons from the electrode to hydrogen ions in the solution (*e.g.* Gurney's theory).¹ As Gurney has pointed out, this mechanism is essentially irreversible.

(B) The primary act is the transfer of hydrogen ions from the solution to adsorption places on the electrode, followed by their evaporation as molecular pairs from the surface,² *viz.* :



¹ Gurney, *Proc. Roy. Soc., A*, 1931, **134**, 137.

² Frumkin, *Acta physicochemica, U.S.S.R.*, 1935, **2**, 505 ; Polanyi and Horiuti, *Z. physikal. Chem., A*, 1933, **164**, 121.

When the metal surface is also in adsorptive equilibrium with the hydrogen atmosphere this process is completely reversible.

We shall take the view, which will be supported in detail in another publication, that at high overvoltage (irreversible) electrodes the process which occurs is of type A, while that at reversible electrodes (platinised or activated platinum, etc.) is of type B. With some metals of low overvoltage, both processes may contribute to the current.

It is probable that adsorbed hydrogen is present on the surface of the metal in both cases, the essential difference between electrodes of the two types being in the rate of desorption. For adsorbed hydrogen can be liberated, on account of its lower potential energy, at a less negative potential than is required by Gurney's mechanism; hence, when a current is passed it is to be expected that adsorbed hydrogen will first be liberated.

The amount of adsorbed hydrogen will continue to increase until either the rate of desorption is equal to its rate of formation, when an equilibrium state will be established and hydrogen will continue to be liberated by mechanism B, or if the rate of desorption is insufficient the surface will become saturated and the potential will rise to the point at which process A can take place. Although it is easy to demonstrate the formation of adsorbed oxygen prior to the establishment of the oxygen overvoltage, the formation of adsorbed hydrogen at metals of high overvoltage has not been experimentally demonstrated, but it is clearly a possibility which must be taken into account.

On these views, it follows that little or no atomic hydrogen is formed at reversible electrodes, and only those reductions can be brought about which are effected by adsorbed hydrogen. At high overvoltage electrodes, the reductions might be effected either by free or adsorbed hydrogen. But if the reaction is a purely secondary one between free hydrogen and the reducible substance, in the absence of disturbing factors the potential of the electrode will be that at which hydrogen is normally liberated in the absence of the substance. But if the substance is adsorbed on the electrode surface, the effective area of the latter may be reduced and the potential thereby displaced in the negative direction. If the reduction occurs at potentials below the hydrogen overvoltage, the process may be effected by either adsorbed hydrogen or by direct electron transfer.

It has frequently been stated that the energy of the liberated hydrogen is greater, the greater the overvoltage at which it is produced. This is only true in the limited sense that free atomic hydrogen has a greater potential energy than adsorbed hydrogen, but in a series of high overvoltage metals it does not appear to be necessary that the potential energy of the hydrogen should be greater the greater the overvoltage, for the latter is the potential difference which is required to raise the electron levels of the metals by a sufficient amount to enable the transfer to take place. It is probable also that adsorbed hydrogen at reversible electrodes is in a more reactive condition than that at inert electrodes at which the rate of desorption is slow.

These distinctions are supported by a broad survey of the facts. Difficulty reducible compounds require a high overvoltage cathode, *i.e.* they are effected by atomic hydrogen. The reduction of unsaturated compounds, on the other hand, is usually more readily brought about at platinised and similar electrodes. For example, the reduction of cinnamic acid is small at a bright platinum electrode, but occurs readily at

electrodes coated with nickel or palladium black. This is evidently a case of reaction with adsorbed hydrogen, and it would appear that it only differs from the catalytic hydrogenation in that the hydrogen is produced on the electrode surface.

Experimental.

These experiments were designed to give illustrative examples of the various types of reduction processes. Some of the cases chosen have already been extensively investigated, but the earlier workers were usually more interested in the products of the electrolysis than the conditions and in many cases very little information is available as to the potentials at which the reduction takes place.

The experimental arrangements were similar to those described in Part II.³ The solutions were freed from oxygen by bubbling a stream of purified nitrogen or hydrogen. With mercury electrodes it was found that erratic oscillations of the potential occurred unless hydrogen was used and the electrode given a short cathodic polarisation during the introduction of the solution to the cell. The electrodes used had an approximate apparent area of 2 cm.² The lead was A.R. (As free) quality, and fresh electrodes were prepared for each set of experiments. The standard electrode was mercurous sulphate in *N* sodium sulphate ($E_0 = +0.67$). In this paper the potentials have been converted to the hydrogen scale.

Acetone.—Elbs and Brand⁴ found that acetone was reduced at a lead cathode, the reduction products being mainly isopropyl alcohol and pinacol. Under certain conditions, and particularly at cadmium electrodes, propane and metal alkyls can be formed.⁵ Hibbert and Read⁶ found that the lowering of the cathodic potential produced by acetone was about 0.05 volt. Experiments were made with lead electrodes on *M*/10 acetone in *M*/10 sulphuric acid, and it was found that the current-potential curve (taken from $i = 20$ to 5200×10^{-6} amps.) was practically unaffected by the addition of acetone, the depression of the potential amounting at most to 4 millivolts. The reduction of acetone at this electrode is thus a purely secondary process, and is to be regarded as a reaction with atomic hydrogen. The low efficiency of the reduction⁶ and the nature of the products are in agreement with this view.

Sodium Formate.—At a lead electrode in alkaline solution containing *M*/100 formate there was no essential displacement of the current-potential curve, even with very small current, at first, and no sign of concentration polarisation. That reduction occurred was shown by the formation of a white film (probably paraformaldehyde) on the surface of the electrode, which in successive runs caused the potential to be displaced towards more positive values. This reduction is therefore probably also a secondary reaction with atomic hydrogen. Owing to the film formation it was not studied in detail.

Pyridine is readily reduced to piperidine in acid solutions at lead and mercury cathodes.⁷ The addition of hydrogen carriers which are effective in other reductions has no effect, but it has been found that the presence of colloidal platinum, prepared by Bredig's method and the addition of a small percentage of palladium chloride reduced the current-efficiency at mercury from 40 to 8 per cent.⁸

It was found that at a mercury cathode the current-potential curve (taken from $i = 13$ to 1200×10^{-6} amps.) was scarcely affected by the

³ Butler and Leslie, this vol., p. 435.

⁴ Elbs and Brand, *Z. Elektrochem.*, 1902, 8, 783.

⁵ Tafel and Schepps, *ibid.*, 1911, 17, 972.

⁶ Hibbert and Read, *J. Amer. Chem. Soc.*, 1924, 46, 983.

⁷ Ahrens, *Z. Elektrochem.*, 1895, 2, 577.

⁸ Zappi, *Anal. soc. quim. Argentina*, 1915, 3, 433.

presence of pyridine ($M/10$), so that this reduction is also a secondary one produced by atomic hydrogen. The observations quoted above indicate that the reduction is not brought about by adsorbed hydrogen for the effect of colloidal platinum and the deposition of palladium is to produce an adsorbent surface.

An interesting and novel phenomenon was observed with bright platinum electrodes. Fig. 1 shows the current-potential curves obtained with various concentrations of pyridine in $M/10$ sulphuric acid. Even

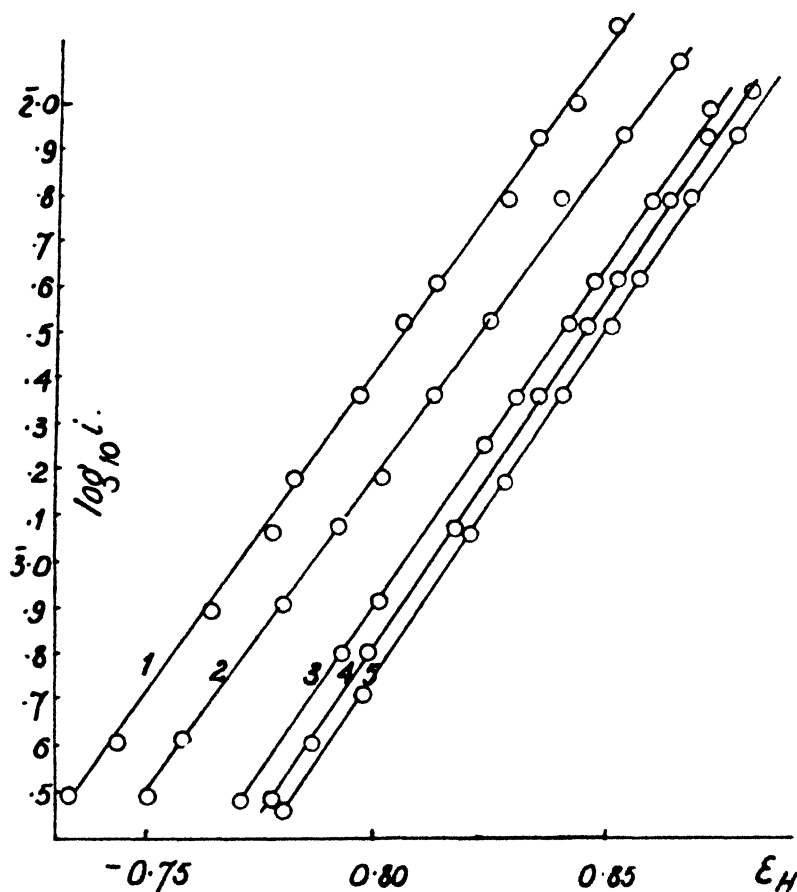
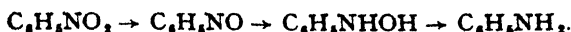


FIG. 1.—Current-potential curves for pyridine in $M/10$ H_2SO_4 at Pt cathode. (1) H_2SO_4 alone; (2) + $M/10,000$; (3) + $M/1000$; (4) + $M/100$; (5) + $M/10$ pyridine.

very small concentrations of pyridine cause a displacement of the whole curve in the negative direction. This is apparently due to the electrocapillary adsorption of the pyridine on the electrode. No adsorption occurs at mercury, but the potential in this case is considerably more negative than at platinum, and it is known that capillary active substances which are adsorbed on mercury in the neighbourhood of the "null" point are almost completely displaced from the surface at more negative potentials.⁹

⁹ Butler, *Proc. Roy. Soc., A*, 1929, **122**, 399.

Nitrobenzene.—The reduction of nitrobenzene has been extensively studied by Haber and Russ and the former showed¹⁰ that the main reaction occurs in the following successive stages :



Under appropriate conditions side reactions between these intermediates may give rise to azoxybenzene, hydrazobenzene or azobenzene. The reduction takes place at a considerably more positive potential than that at which hydrogen is liberated in the absence of nitrobenzene. Russ¹¹ investigated the dependence of the potential on the current and concentration of nitrobenzene and his results are referred to in the discussion.

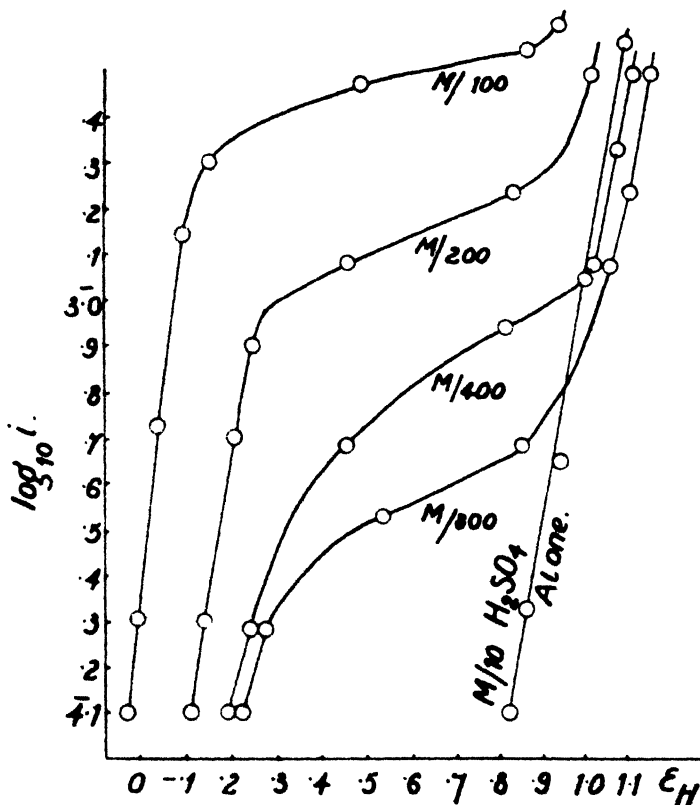


FIG. 2(a).—Current-potential curves for nitrobenzene in $M/10 \text{ H}_2\text{SO}_4$; mercury cathode.

Russ's measurements were made with comparatively concentrated solutions of nitrobenzene in alcoholic solution and in the range of currents used show no transition to a higher potential. When dilute aqueous solutions are used there is a transition current above which the potential rises to the neighbourhood of the hydrogen overvoltage. Fig. 2(a) shows some current-potential curves obtained in $M/10$ sulphuric acid with a mercury cathode. It has been suggested¹² that in the case of irreversible reductions the transition is not due to the depletion of the depolariser at the electrode,

¹⁰ Haber, *Z. Elektrochem.*, 1898, 4, 506; *Z. physikal. Chem.*, 1900, 32, 271.

¹¹ Russ, *ibid.*, 1903, 44, 641.

¹² Cf. Glasstone and Hickling's *Electrolytic Oxidation and Reduction*, 1935, p. 192.

but to the slowness of the reaction between hydrogen and the depolariser (*i.e.* there is a maximum rate of the reaction for a given concentration of

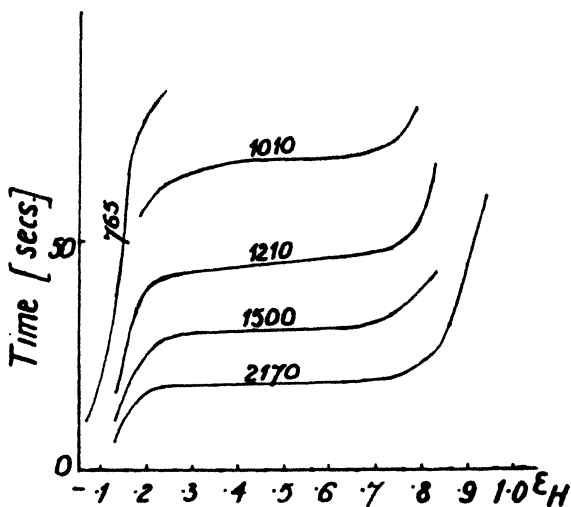


FIG. 2(b).—Time-potential curves for nitrobenzene (M/200), in M/10 H_2SO_4 . Numbers refer to current in micro-amps.

the depolariser, and if the current exceeds this value, hydrogen accumulates at the electrode and causes the potential to rise to the potential at which it is liberated). It has been shown that the transition current is not a very precise quantity and more exact information is obtained from the potential-time curves with constant currents (Fig. 2(b)). These showed transitions of exactly the same type as those obtained in the reversible reduction of hydroquinone, etc., and Fig. 3 shows that they obey the

relation $it = i_0 t + \alpha$ (where t is the transition time and i_0 and α are constants), which has been found to hold for numerous cases in which the

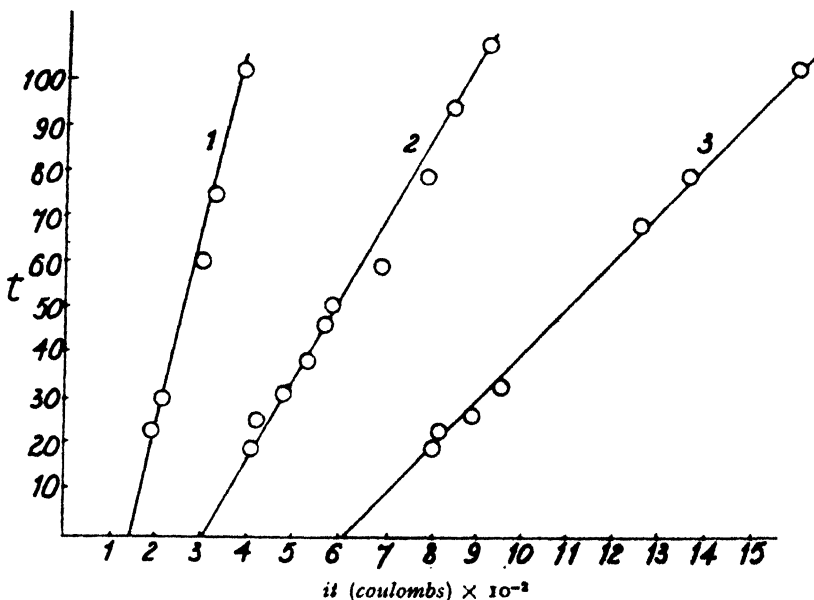


FIG. 3.—Effect of concentration of nitrobenzene on the length of the cathodic break. (1) M/400; (2) M/200; (3) M/100.

transition is undoubtedly due to concentration polarisation.¹³ The constants i_0 and α , given in Table I., are approximately proportional to

¹³ Armstrong and Butler, *Proc. Roy. Soc., A*, 1933, 139, 406.

the concentration of nitrobenzene. The transition in this case is thus probably due to the depletion of the depolariser at the electrode.

It is also to be observed that neither the current-potential nor the time-potential curves show any signs of consecutive processes, which would be the case if any of the primary products of the reduction were reduced at a more negative potential than nitrobenzene. Haber has shown that it is possible by controlling the potential of the electrode to obtain different reduction products. It is unlikely that this is a direct result of the variation of the

TABLE I.—VALUES OF i_0 AND α IN $(i - i_0)$
 $i = \alpha$ FOR AQUEOUS SOLUTIONS OF NITRO-
 BENZENE. (c , CONCENTRATION IN MOL./
 LITRE; α IN COULOMBS $\times 10^{-12}$, i_0 IN
 AMPS. $\times 10^{-6}$.)

c .	α .	i_0 .
0.01	6.2	810
0.005	3.0	380
0.0025	1.5	190

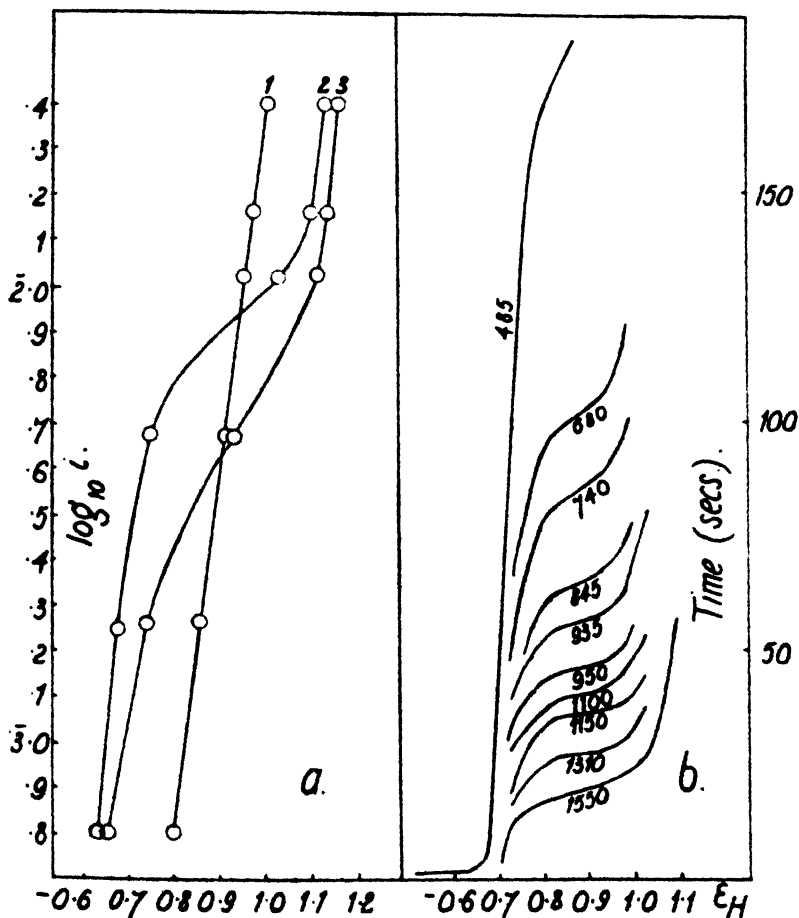


FIG. 4.—Benzaldehyde at mercury cathode. (a) Current-potential curves: (1) M/10 H_2SO_4 alone; (2) + M/50 $C_6H_5 \cdot CHO$; (3) + M/100 $C_6H_5 \cdot CHO$. (b) Time-potential curves of M/100 $C_6H_5 \cdot CHO$. Numbers refer to current in micro-amperes.

potential, although it may arise from secondary effects. For example, if the current employed is above the transition value, so that the potential

is near the hydrogen over-voltage, reduction by atomic hydrogen may occur, for the depolariser will still reach the electrode at the maximum rate of diffusion and may when reduced in this way give rise to different products than those at the lower potential.

Benzaldehyde.—The reduction of benzaldehyde ¹⁴ also takes place at more positive potentials than the hydrogen overvoltage, but the displacement at mercury is comparatively small. Fig. 4(a) shows the current-potential curves of solutions in *M*/10 sulphuric acid with a mercury electrode. These show a transition, the upper part of the curve being on the right of the hydrogen overvoltage line. This indicates the adsorption of the reduction products on the surface. Notwithstanding the small rise of potential-time curves, examples of which are shown in Fig. 4(b) show a well-defined transition, and the transition times for a given solution are related to the current by $it = i_0t + \alpha$, but in this case the constants i_0 and α were found to be not proportional to the concentration.

Discussion.

The following cases have been observed : (1) the potential at which electrolysis takes place is unaffected by the reducible substance (acetone and sodium formate at lead, pyridine at mercury) ; (2) electrolysis occurs at potentials more positive than those required for the liberation of hydrogen in the absence of the depolariser (nitrobenzene and benzaldehyde at mercury) ; (3) the substance causes a displacement of the potential in the negative direction. In (1) the process is evidently a purely secondary reaction of the reducible substance with free atomic hydrogen. In (2) there are two possibilities, (a) reaction of the depolariser with adsorbed hydrogen, (b) reduction by the direct transfer of electrons from the electrode to the depolariser. It does not appear to be possible at present to make a definite decision between these two modes.

In the theory of electrolytic reduction proposed by Haber and Russ,¹⁵ which was designed to account for cases of this kind, it was supposed that the depolariser reduced the effective concentration of hydrogen at the electrode and thereby depressed the potential in accordance with the equation

$$E = E^{\circ} + \frac{RT}{F} \log \frac{H^+}{[H]} \quad (1)$$

where $[H]$ is the effective concentration of (atomic) hydrogen at the electrode. The concentration of hydrogen is determined by equilibrium between its rate of formation (i) and its rate of reaction with the depolariser D , which taking the stoichiometrical equation of the reaction as $D + nH \rightarrow DH_n$ was assumed to be $k[D][H]^n$. Hence

$$E = E^{\circ} + \frac{RT}{nF} \log \frac{k[D][H^+]}{i}$$

Haber and Russ found that the variations of E with the concentration of the depolariser and with the current (i) was reasonably in accordance with an expression of the type

$$E = E^{\circ} + x \log \frac{[D]}{i}$$

¹⁴ Law, *J. Chem. Soc.*, 1906, 89, 1512 ; 1907, 91, 748 ; 1911, 99, 113.

¹⁵ *Loc. cit.*, ref. (11) ; Haber and Russ, 1904, 47, 257.

when x has values which are closer to that required for $n = 1$ than for the stoichiometrical value of n . For example, in the reduction of nitrobenzene in alkaline solutions at platinum, gold and silver, x varied from 0.048 to 0.054, and in acid solutions at platinum and gold from 0.053 to 0.075.

Haber and Russ's derivation assumes that the electrode functions as a reversible hydrogen electrode which is certainly incorrect with ordinary smooth electrodes.¹⁶ Now, as has been pointed out, it is possible that adsorbed hydrogen may be formed at potentials below the normal overvoltage which might react with the depolariser in this way, but at an irreversible electrode the potential would not be related to the amount of adsorbed hydrogen by a relation like (1). It is therefore very doubtful whether the Haber and Russ relation would be obtained at an irreversible electrode even if the reduction took place by the formation of adsorbed hydrogen below the normal overvoltage and its reaction with the depolariser.

A relation of the type

$$E = E^\circ + \frac{RT}{F} \log \frac{D}{i}$$

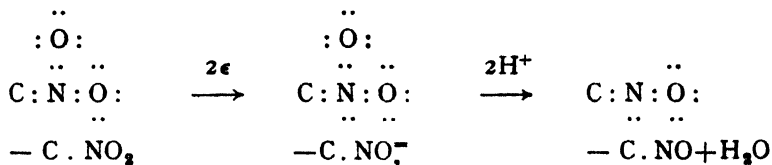
is also to be expected when the process is a direct electron transfer from the electrode to the depolariser. (For the discharge of hydrogen ions an expression of this kind is obtained, the factor before the logarithm being $2RT/F$; but the reasons for the factor 2 given in Gurney's theory will not apply to the transfer to a heavy molecule.) The fact that the experimental data are in reasonable agreement with this expression is an argument in favour of the direct reduction.

It has been suggested that the molecules which are reduced by a direct electron transfer are those which give rise to *reversible* oxidation potentials. But it is not necessary that a reversible potential should be established in every such case. The condition of reversibility is that there shall be a single potential at which electron transfers can take place from the electrode to the substance and from its reduction product to the electrode at the same and not inappreciable rate. The condition of transfer of electrons from the electrode to a molecule in solution is approximately stated as $\phi + V < I_R$, where ϕ is the thermionic work function of the metal, V the potential difference, and I_R the electron affinity of the substance (taking account of any solvation and adsorption energies). The condition for the reverse process is $I_O < \phi + V$, where I_O is the ionisation potential of the oxidised form of the substance. In practice, if the two processes are to occur at the same potential it is necessary that I_O should be of nearly the same magnitude as I_R , i.e. the energy required to remove electrons from the oxidised form should be about the same as the electron affinity of the reduced form of the substance. Now, if the primary product of the reduction undergoes irreversible changes, this condition will not be satisfied and reduction may occur by direct electron addition without giving rise to a reversible potential.

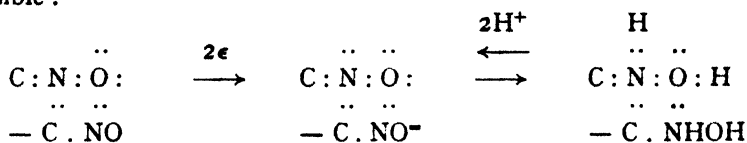
It is not unreasonable to suppose that substances like nitrobenzene may have an electron affinity which enables them to act as electron acceptors. The nitrogen atom in nitrobenzene has an incomplete shell of electrons, and the process of reduction might occur by the gain of two

¹⁶ Cf. Butler and Armstrong, *J. Chem. Soc.*, 1934, 743.

electrons, giving the ion $\text{C}_6\text{H}_5\text{NO}_2^-$, which by an irreversible reaction with hydrogen ions gives nitrosobenzene, the first product of the reduction, *viz.*:



A similar process can then occur again, but in this case it is believed to be reversible:



The reduction of the hydroxylamine to aniline apparently requires a more negative potential and may be a reduction by atomic hydrogen. It is interesting to observe that Conant¹⁷ has suggested a similar mechanism for the reduction of hydroxylamine by ionic reducing agents.

We conclude that in these cases it is not improbable that the reduction is effected by the direct transfer of electrons from the electrode to the depolariser, but we cannot exclude definitely the possibility of reaction with adsorbed hydrogen which might be formed below the normal hydrogen overvoltage. A definite decision on this point must await the discovery of the conditions of formation and properties of adsorbed hydrogen on high overvoltage metals.

Summary.

1. The possible modes of electrolytic reduction are reviewed and their distinguishing characteristics discussed.

2. Examples are given of various types. Acetone, sodium formate and pyridine at lead electrodes cause no significant displacement of the hydrogen overvoltage curve over the whole range, and are reduced by free atomic hydrogen. Nitrobenzene and benzaldehyde are reduced at mercury at more positive potentials than those at which hydrogen is liberated in their absence. With larger currents a transition occurs to near the hydrogen overvoltage. The time-potential curves show no sign of consecutive processes, and obey the relation $(i - i_0)t = \alpha$, which is characteristic of many cases in which the transition is due to the slow diffusion of the depolariser to the electrode. It is concluded that it is not improbable that these reductions are effected by direct transfer of electrons from the electrode, although reduction by adsorbed hydrogen, liberated below the normal overvoltage, cannot be definitely excluded. The adsorption of the substance on the electrode, which may displace the hydrogen overvoltage in the negative direction is illustrated by pyridine at platinum.

We thank Messrs. Imperial Chemical Industries for their grant.

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¹⁷ Conant and Lutz, *J. Amer. Chem. Soc.*, 1923, 45, 1047.

THE KINETICS OF THE NITRITE-IODINE REACTION.

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Of the many thermal reactions of halogens in liquid solution, only a few are known in which it is presumed that halogen atoms play an essential rôle. Such are the reversible formation and decomposition of ethylene iodide in CCl_4 solution,¹ and the reactions in aqueous solution between oxalates and iodine.^{2, 3, 4} For various reasons we thought it likely that the reactions between nitrites and iodine in aqueous solution might also involve the intermediacy of iodine atoms. The thermal reaction between KNO_2 and iodine has previously been studied by Berthoud and Berger⁵ in connection with their study of the photochemical process, but only a few observations were made and the data obtained were insufficient to establish the mechanism. We have therefore re-investigated this thermal reaction—using both KNO_2 and NaNO_2 as reactants—under a wider range of experimental conditions, and have evolved a mechanism which accounts quantitatively for our results. This mechanism, which introduces iodine atoms or combinations of iodine atoms with iodide ions (I_2^- ions), is further supported by the results of experiments in which nitrite and oxalate react simultaneously with iodine. It also links up quantitatively the rate of the nitrite-iodine reaction with the rate of decomposition of HNO_2 in aqueous solution, exhaustively investigated by Abel and his collaborators.⁶

Experimental.

Kinetic measurements have been carried out at 40°, 50° and 60° with NaNO_2 (and KNO_2) and I_2 as reactants. The reaction could only be studied over a limited range of p_{H} , since with too alkaline solutions appreciable loss of iodine by iodate formation occurs, and with solutions too acid complications are caused by the decomposition of free nitrous acid. The actual range of p_{H} over which it is permissible to neglect these disturbing processes depends not only on the temperature and the concentrations of reactants, but very markedly also on the concentration of free iodide; roughly, however, a suitable range of p_{H} for the isolation of the reaction between NO_2^- and I_2 is given by the use of phosphate buffers, as already employed by Berthoud and Berger.⁵ These authors have shown that the reaction rate under their experimental conditions is independent of p_{H} , at least over the range covered by a variation of $[\text{HPO}_4^{--}]/[\text{H}_2\text{PO}_4^-]$ from 0.33 to 3. We, too, have found that for each set of experimental

¹ Polissar, *J. Am. Chem. Soc.*, 1930, **52**, 756.

² Berthoud, *Trans. Faraday Soc.*, 1931, **27**, 527; *Helv. Chim. Acta*, 1933, **16**, 393.

³ Griffith and McKeown, *Trans. Faraday Soc.*, 1932, **28**, 752.

⁴ Abel and Hilferding, *Z. physikal. Chem.*, A, 1935, **172**, 353.

⁵ Berthoud and Berger, *J. Chim. physique*, 1928, **25**, 542.

⁶ Abel *et al.*, *Z. physikal. Chem.*, A, 1928, **132**, 55; 1928, **134**, 279; 1928, **136**, 135, 419, 430; 1930, **148**, 337.

conditions (concentrations of reactants and of iodide) there is a more or less limited range of p_H within which the process measured is exclusively $\text{NO}_2^- + \text{I}_2 + \text{H}_2\text{O} \rightarrow \text{NO}_3^- + 2\text{H}^+ + 2\text{I}^-$, and whose velocity is independent of $[\text{H}^+]$. In most of our experiments phosphate buffers were employed; in addition, a few measurements have been effected in NaHCO_3 solutions saturated with CO_2 and in acetate buffers. The reaction rate was found to be dependent also on ionic environment; hence, in order to make legitimate comparisons the ionic strength (μ) in various series was kept approximately constant by addition of NaClO_4 , NaNO_3 or KNO_3 .

All the chemicals used were of A.R. quality. Reaction mixtures of high iodide content were contained in glass-stoppered flasks; samples withdrawn from time to time were run into excess of sodium arsenite solution and their iodine contents obtained by back-titration with standard iodine solution. This procedure is, however, not accurate enough when the iodide content is low (less than 0.03 *M*), owing to progressive loss of iodine by volatilisation; under these circumstances, a number of 20 c.c. samples were sealed in thin glass tubes (of about 30 c.c. capacity) at room temperature, and these were simultaneously immersed in the thermostat at 50° or 60°. From time to time a tube was withdrawn, rapidly cooled, then broken and the iodine estimated as before. In all cases light was rigidly excluded from the reacting system.

In formal agreement with the results of Berthoud and Berger, the reaction was found to be unimolecular with respect to iodine, but not of simple order with respect either to nitrite or to iodide (which retards the reaction). The order with respect to nitrite ($n_{\text{NO}_2^-}$) lies between the limits of 1 and 2, approaching the lower limit when $[\text{I}^-]$ is very small compared with $[\text{NO}_2^-]$ and the upper limit when $[\text{I}^-]$ is large. The order with respect to iodide (n_{I^-}) is similarly dependent not only on the concentration of iodide, but also on that of nitrite. For a given concentration of nitrite n_{I^-} varies from between 0 and -1 at low $[\text{I}^-]$ to a limit of -3 at high $[\text{I}^-]$. If we provisionally define the rate of reaction by the equation

$$-\frac{d[\Sigma\text{I}_2]}{dt} = \frac{k'[\text{NO}_2^-][\Sigma\text{I}_2]}{K_2 + [\text{I}^-]} \quad (1)$$

where $[\Sigma\text{I}_2]$ = concentration of total titratable iodine, $[\text{I}^-]$ = concentration of free iodide, and $K_2 = \frac{[\text{I}^-][\text{I}_2]}{[\text{I}_2^-]}$ is the equilibrium constant of triiodide formation, the above statements may be reworded in the sense that k' is constant at low $[\text{I}^-]$ and high $[\text{NO}_2^-]$, but decreases progressively as $[\text{I}^-]$ is increased, finally becoming proportional to $[\text{NO}_2^-]/[\text{I}^-]^2$. Search for a kinetic expression to fit these findings led to the following empirical expression:

$$-\frac{d[\Sigma\text{I}_2]}{dt} = \frac{k[\text{NO}_2^-][\Sigma\text{I}_2]}{\{K_2 + [\text{I}^-]\} \left\{ A \frac{[\text{I}^-]^2}{[\text{NO}_2^-]} + 1 \right\}} \quad (2)$$

or
$$k' = \frac{k}{A \frac{[\text{I}^-]^2}{[\text{NO}_2^-]} + 1} \quad (3)$$

where k and A are constants (at constant temperature) independent of $[\text{NO}_2^-]$ and of $[\text{I}^-]$.

Equations (2) and (3) are found to be in excellent agreement with our kinetic data over a wide range of variation of $[\text{NO}_2^-]$ and $[\text{I}^-]$, so long as the total ionic strength of the various reaction mixtures is maintained constant. The value of k' at constant $[\text{NO}_2^-]$ and constant $[\text{I}^-]$ is, however, sensitive to change in μ , decreasing progressively as μ is increased. Most of our experiments have been carried out at $\mu \approx 0.7$ and $\mu \approx 2.7$. In the former event the ionic strength is made up of contributions from

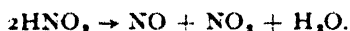
NaNO_3 , KI , Na_2HPO_4 and KH_2PO_4 . For $\mu \approx 2.7$, reaction mixtures are also $2M$ with respect to NaNO_3 . Kinetic measurements with intermediate concentrations of NaNO_3 showed that, so far as this salt is concerned, a simple relation holds over the whole range of $[\text{NaNO}_3]$ from $[\text{NaNO}_3] = 0$ to $[\text{NaNO}_3] = 2.0$ between k' and μ , *viz.*,

$$\log k'_\mu - \log k'_{\mu_1} = 0.153 (\mu_1 - \mu) \quad (4)$$

This same dependence of k' on μ obtains at very different values of $[\text{I}^-]^2/[\text{NO}_2^-]$, from which it follows that it is the constant k , and not A , which is sensitive to μ .

We have used equation (4) to correct the velocity coefficients k' obtained in the series $\mu \approx 0.7$ and $\mu \approx 2.7$ to the values k'_{corr} . they should have at $\mu = 0.7$ and 2.7 respectively. This procedure is not free from criticism, since equation (4) only represents the neutral salt effect of NaNO_3 upon k' , whereas the individual k' 's in each series should really be corrected not for varying NaNO_3 , but for the neutral salt effects of NaNO_3 , KI , Na_2HPO_4 , and KH_2PO_4 which may well be different from that of NaNO_3 . The corrections applied, however, are in most cases only a few per cent. in the two series, so that the values of k'_{corr} cannot be seriously in error on this account.

Before tabulating our experimental results, it is first necessary to discuss in more detail the conditions of acidity under which the reaction is not interfered with by side reactions. With solutions too alkaline, especially in the presence of low $[\text{I}^-]$, loss of iodine by iodate formation may ensue in presence or absence of nitrite. Blank experiments were made in absence of nitrite to determine at 50° and 60° and at various concentrations of iodide the lower limit of $[\text{H}^+]$ at which this disturbing effect may safely be ignored. On the other hand, the reaction mechanism is indubitably changed if an upper limit of $[\text{H}^+]$ be exceeded. This is primarily due to the decomposition of free nitrous acid according to



This has the effect that with high iodide concentrations the liberated NO_2 reacts with iodide to give iodine (and NO is evolved), so that I_2 is formed in systems not initially containing iodine, and hence a spuriously low rate for disappearance of iodine would be obtained. At low iodide concentrations, however, this effect may be negligible, but on the other hand the NO liberated reacts with iodine to give a spuriously high rate of disappearance of I_2 . We have thus been forced to work between rather narrow limits of p_{H} which are about $p_{\text{H}} = 6$ for low concentrations of iodide and $p_{\text{H}} = 7$ for high concentrations of I^- . In all cases where any doubt might exist, the $[\text{H}^+]$ was varied over at least a two-fold range to test for the absence of the above-mentioned side reactions. It should further be noticed that the presence of NaNO_3 , NaClO_4 and other neutral salts causes considerable increase in the acidity of phosphate buffers. For example, addition of $2.0 M$ NaNO_3 to a phosphate buffer in which $[\text{Na}_2\text{HPO}_4]/[\text{KH}_2\text{PO}_4] = 0.1/0.1$ or $0.15/0.03$ causes a fall in p_{H} of about 0.6 units. Hence, in the presence of appreciable quantities of one of these neutral salts the phosphate ratio $[\text{Na}_2\text{HPO}_4]/[\text{KH}_2\text{PO}_4]$ cannot safely be reduced to as small a value as in absence of the salt.

In Table I. are given the results of kinetic experiments at 50° and 60° with NaNO_3 and I_2 as reactants in the presence of phosphate buffers. Tables I.(a) and (c) refer to an ionic strength of 0.7 (no added NaNO_3), and Tables I.(b) and (d) to $\mu = 2.7$ (*i.e.* with $2.0 M$ NaNO_3 added). The initial iodine content was $0.0027M$ or $0.001M$ in most cases. The tables give the mean values of k' as defined by equation (1) and of k'_{corr} , the values of k' corrected to $\mu = 0.7$ or 2.7 by means of equation (4) as already explained. In evaluating k' we have employed for K_2 the values 0.00225 and 0.0026 at 50° and 60° respectively; as shown by the work of Kiss and

Urmánczy,⁷ these may be taken as practically independent of μ over the range of $[\text{NaNO}_2]$ studied. Each of the five or six values of k' given by each experiment was obtained from equation (1) written in the form

$$k' = \frac{k_{\text{uni}}\{K_2 + [\text{I}^-]_{\text{m}}\}}{[\text{NO}_2^-]_{\text{m}}}$$

where k_{uni} is the unimolecular velocity coefficient (time in minutes) with respect to iodine, and $[\text{I}^-]_{\text{m}}$ and $[\text{NO}_2^-]_{\text{m}}$ are mean values of $[\text{I}^-]$ and $[\text{NO}_2^-]$ over the relevant time interval. Since, under our experimental conditions, the coefficient k' is sensibly constant in each experiment, we give only the average value of k' in each experiment together with the average value of $[\text{I}^-]_{\text{m}}/[\text{NO}_2^-]_{\text{m}}$. Values of $[\text{I}^-]$, the concentration of free iodide during an experiment, have been evaluated from the initial concentrations of potassium iodide (c or $[\text{KI}]_0$), and of iodine (a) and the extents of reaction (x) by means of the equation

$$[\text{I}^-] = \frac{1}{2}\{(c - a - K_2 + 3x) + \sqrt{(c - a - K_2 + 3x)^2 + 4K_2(c + 2x)}\}.$$

For each of these four series of experiments a plot of the reciprocal of $k'_{\text{corr.}}$ against $[\text{I}^-]^2/[\text{NO}_2^-]$ is found to give a straight line. This is illustrated for one of the series, that of Table I.(d), in Fig. 1. In the plot are also included data from additional experiments, which for brevity have been omitted from Table I.(d). The linearity of the plots of $1/k'$ against $[\text{I}^-]^2/[\text{NO}_2^-]$ shows that equation (3) holds (at constant ionic strength) over the whole range of variation of $[\text{I}^-]$, $[\text{NO}_2^-]$ and $[\text{H}^+]$ covered by Table I. From the plots, or by applying the method of least squares, the

TABLE I.

$\frac{[\text{Na}_2\text{HPO}_4]}{[\text{KH}_2\text{PO}_4]}$	$[\text{NaNO}_2]_0$	$[\text{KI}]_0$	$\left\{ \frac{[\text{I}^-]_{\text{m}}}{[\text{NO}_2^-]_{\text{m}}} \right\} \times 10^3$ av.	$k' \times 10^3$	$k'_{\text{corr.}} \times 10^3$
(a) Temp. = 50°; $[\text{NaNO}_2] = 0$; $\mu = 0.7$					
0.05/0.2	0.1807	0.002	0.04	29.0	27.4
0.05/0.2	0.1807	0.01	0.50	26.7	25.3
0.1/0.2	0.1807	0.015	1.09	23.7	23.7
0.1/0.1	0.3614	0.035	3.09	18.8	19.5
0.1/0.1	0.1807	0.03	4.46	17.5	17.0
0.1/0.1	0.1807	0.035	6.14	15.0	14.6
0.1/0.1	0.1807	0.04	8.04	13.1	12.8
0.1/0.1	0.1807	0.045	10.20	11.5	11.2
0.1/0.1	0.1807	0.05	12.64	10.0	9.75
0.1/0.1	0.1807	0.06	18.59	7.4	7.25
(b) Temp. = 50°; $[\text{NaNO}_2] = 2.04$; $\mu = 2.7$					
0.12/0.12	0.1807	0.002	0.03	13.70	13.70
0.12/0.12	0.1807	0.01	0.50	12.70	12.70
0.1/0.1	0.1816	0.015	0.98	12.15	11.90
0.1/0.1	0.1816	0.02	1.86	10.95	10.75
0.15/0.03	0.3635	0.03	2.24	9.50	10.25
0.1/0.1	0.1816	0.025	3.16	9.25	9.08
0.1/0.1	0.1816	0.03	4.34	8.35	8.21
0.15/0.03	0.3635	0.045	5.30	6.60	7.14
0.12/0.03	0.1807	0.035	6.18	7.14	7.01
0.12/0.03	0.1807	0.04	8.20	6.13	6.03
0.15/0.03	0.3635	0.06	9.34	5.00	5.45
0.12/0.03	0.1807	0.045	10.34	5.26	5.18
0.15/0.03	0.3635	0.07	12.73	4.15	4.54
0.2/0.02	0.1807	0.05	12.83	4.25	4.54

⁷ Kiss and Urmánczy, *Z. anorg. allg. Chem.*, 1931, **202**, 172.

TABLE I.—*continued*.(c) Temp. = 60°; [NaNO₃] = 0; $\mu = 0.7$.

0.05/0.2	0.1807	0.002	0.04	119.5	112.5
0.02/0.08	0.0904	0.002	0.08	135.2	114.6
0.05/0.2	0.1810	0.007	0.35	116.6	110.2
0.05/0.2	0.1810	0.01	0.60	114.0	107.7
0.05/0.2	0.1810	0.015	1.30	104.8	99.3
0.1/0.2	0.1805	0.03	4.93	65.9	65.7
0.1/0.1	0.1810	0.045	10.92	46.6	45.4
0.1/0.2	0.1807	0.05	13.20	38.5	38.9
0.1/0.1	0.1810	0.06	18.89	31.8	31.1
0.1/0.1	0.1814	0.07	25.41	25.0	24.5
0.1/0.1	0.1814	0.08	33.41	19.8	19.5
0.1/0.1	0.1814	0.09	42.38	16.1	16.0
0.1/0.1	0.1814	0.10	52.48	13.5	13.4

(d) Temp. = 60°; [NaNO₃] = 2.04; $\mu = 2.7$.

0.12/0.12	0.1807	0.002	0.04	56.5	56.5
0.1/0.2	0.0904	0.004	0.20	58.5	57.2
0.12/0.12	0.1807	0.01	0.63	54.2	54.2
0.1/0.1	0.0904	0.015	2.32	46.0	43.6
0.1/0.1	0.1807	0.03	4.51	35.2	34.6
0.15/0.1	0.3586	0.06	9.52	21.8	24.3
0.15/0.03	0.3586	0.07	13.06	18.0	19.7
0.15/0.03	0.0452	0.03	17.05	17.4	16.8
*0.20/0.02	0.5421	0.10	17.83	15.95	15.95
0.15/0.03	0.3628	0.09	21.31	12.45	13.7
0.15/0.03	0.0452	0.035	23.65	13.6	13.15
0.15/0.03	0.3586	0.10	26.70	10.65	11.75
†0.20/0.15	0.7228	0.15	30.29	10.65	10.6
0.15/0.03	0.1807	0.08	33.45	9.90	10.15
0.15/0.03	0.1807	0.09	42.55	8.05	8.30
0.15/0.02	0.1807	0.10	52.86	6.45	6.70
<hr/>					
[NaHCO ₃]					
0.02	0.1807	0.002	0.04	65.6	55.8
0.04	0.1807	0.045	10.40	25.7	22.4
0.10	0.1807	0.084	36.93	9.95	8.95

* [NaNO₃] = 1.44.† [NaNO₃] = 1.20.

constants k and A of equation (3) may be evaluated. The results are shown in Table II., which also includes the result of an experiment at 40° with a low concentration of KI, from which k (but not A) is directly obtained.

TABLE II.

Temp.	μ .	A .	$k \cdot 10^5$.	$k/K_1 = k_1$.
40	2.7	—	2.94	0.0159
50	0.7	153.5	28.4	0.126
50	2.7	160.7	13.8	0.0612
60	0.7	145.7	115.4	0.444
60	2.7	140.2	56.6	0.2175

From these figures we may infer that A is independent of μ and put $A = 157$ at 50° and $A = 143$ at 60°. Further, it is seen that at each temperature k is approximately halved by increasing the ionic strength by 2 units. This result confirms the use of equation (4) for correcting velocity coefficients for changes in μ . The temperature coefficient of k between 50° and 60° is found to be 4.07 at $\mu = 0.7$ and 4.11 at $\mu = 2.7$, or an average of 4.09.

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That NaNO_3 , a resultant of the reaction, exerts none other than an environmental effect on the rate is shown by the experiments of Table III., in which added NaNO_3 is replaced by NaClO_4 .

TABLE III.

$$[\text{NaNO}_3]_0 = 0.1807; [\text{NaClO}_4] = 2.04; \mu \approx 2.7.$$

Temp.	$\frac{[\text{Na}_2\text{HPO}_4]}{[\text{NaH}_2\text{PO}_4]}$	$[\text{KI}]_0$	$\frac{\{[\text{I}^-]_m\}}{[\text{NO}_2^-]_m} \times 10^3, \text{ av.}$	$k' \times 10^4$	$k'_{\text{corr.}} \times 10^4$
50°	0.12/0.12	0.002	0.04	13.9	13.9
60°	0.155/0.015	0.06	18.6	14.7	15.0
60°	0.12/0.12	0.002	0.04	58.3	58.3

Comparison of the values of k' of this table with those of Tables I.(b) and (d) shows that the effects of NaNO_3 and NaClO_4 on the rate are practically identical.

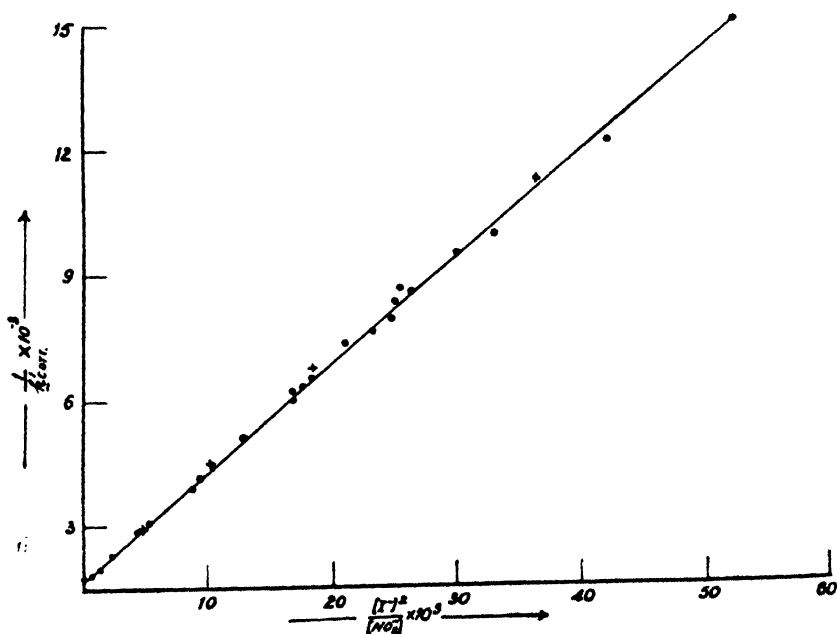


FIG. 1.—● = Phosphate buffers + = Bicarbonate buffers.

We have also carried out a few kinetic measurements at 60° with KNO_3 as the reactant and KNO_2 added to make $\mu = 1.34$. The same mechanism applies as heretofore, as shown by the results of Table IV.

The data of the last three experiments of this table are calculated from the experiments of Berthoud and Berger⁸ under practically the same conditions of ionic strength and acidity; as is seen, they fall into line reasonably with our own results. The plot of $1/k'$ against $[\text{I}]^2/[\text{NO}_2^-]$ for these experiments gives $A = 176$, $k = 107.3 \times 10^{-5}$ and $k_1 = 0.438$. The constants A and k_1 are both about 24 per cent. higher than those calculated (see Table II.) for $\text{NaNO}_3 + \text{NaNO}_2$ at $\mu = 1.34$.

TABLE IV.—TEMP. = 60°; $[\text{Na}_2\text{HPO}_4] = [\text{KH}_2\text{PO}_4] = 0.066$;
 $\mu = 1.34$; $K_3 = 0.00245$.

$[\text{KNO}_2]_0$	$[\text{KNO}_2]$	$[\text{KI}]_0$	$\frac{[\text{I}^-]_m^2}{[\text{NO}_2^-]_m} \times 10^3$ Av.	$k' \times 10^5$
0.96	0.091	0.025	0.74	93.6
0.96	0.066	0.05	2.76	72.5
0.48	0.556	0.04	3.44	67.3
0.48	0.55	0.05	5.27	56.1
0.96	0.041	0.075	6.11	51.9
0.48	0.536	0.06	7.58	46.6
0.24	0.79	0.05	10.28	38.0
1.00	—	0.05	2.6	65.6
1.00	—	0.075	5.9	53.8
1.00	—	0.1125	12.9	32.5

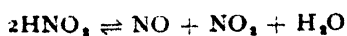
Finally, in Table V. are given some of the results of kinetic measurements in solutions of high acidity, such that appreciable amounts of free nitrous acid are present. Clearly the mechanism which applies to the experiments of Tables I.-IV. no longer suffices.

TABLE V TEMP. 60°, $[\text{NaNO}_2]_0 = 2.04$.

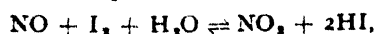
$[\text{Na}_2\text{HPO}_4]/[\text{KH}_2\text{PO}_4]$	$[\text{NaNO}_2]_0$	$[\text{KI}]_0$	$k' \times 10^5$
0.12/0.12	0.18	0.002	50.5
0.07/0.28	0.18	0.002	61 → 63
0.04/0.30	0.18	0.002	91 → 114
0.025/0.25	0.18	0.002	96 → 119
0.03/0.4	0.18	0.002	120 → 194
0.025/0.4	0.18	0.002	140 → 218
0.025/0.4	0.18	0.00133	167 → 275
0.025/0.4	0.18	0.00063	225 → 461
0.025/0.4	0.045	0.002	70 → 76
*0.025/0.4	0.18	0.002	252 → 378

* $[\text{NaClO}_4] = 2.04$ replacing NaNO_3 .

The first experiment in Table V. refers to normal conditions, the remainder to solutions of high acidity. It is seen that in these cases (*i.e.* with low concentrations of I^-), the rate of disappearance of I_2 is greater than the normal, and that the discrepancy increases with increasing acidity, or increasing $[\text{NO}_2^-]$, or diminishing $[\text{I}^-]$. We do not propose to discuss in any detail the mechanism of the reaction under these conditions; further work will be necessary for its elucidation. It appears likely, however, that the chief processes concerned may be represented as



and

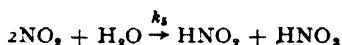
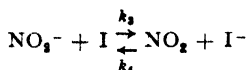
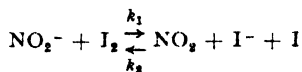


that probably all four reactions are fast ones, that with low values of $[\text{I}^-]$ the rate of the reaction between NO and I_2 is faster than its reversal, and that the rate of disappearance of I_2 is essentially governed by the difference between these two rates.

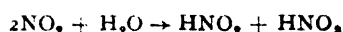
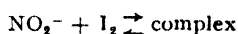
Reaction Mechanism.

Two main types of reaction mechanism can be formulated to give a satisfactory interpretation of our experimental results. These are:—

Mechanism I.



Mechanism II.



In each of these, NO_2 appears as an intermediate, but Mechanism I. involves atomic iodine, whereas Mechanism II. postulates a complex (NO_2I_2^-) between the NO_2^- ion and I_2 . In either case, the net rate of disappearance of iodine equals the rate of formation of nitrate, *viz.*, $k_5[\text{NO}_2]^2$. It should be noted that the reaction between NO_2 and H_2O (velocity coefficient k_5) is also reversible, but under our experimental conditions of low acidity this reversal may be neglected.

Confining attention for the moment to Mechanism I., the usual assumption of stationary state conditions for the intermediates—iodine atoms and NO_2 —leads to the equation

$$k_1k_3[\text{NO}_2^-]^2[\text{I}_2] = k_2k_4[\text{NO}_2]^2[\text{I}^-]^2 + k_2k_5[\text{NO}_2]^3[\text{I}^-] + k_3k_5[\text{NO}_2^-][\text{NO}_2]^2.$$

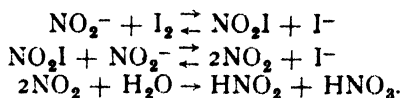
In this we now neglect the second term on the right-hand side compared with the first and the third. This is equivalent to assuming that the rate of reaction 3 is fast compared with that of 2, and the rate of 4 fast compared with that of 5, *i.e.*, that the equilibrium $\text{NO}_2^- + \text{I} \rightleftharpoons \text{NO}_2 + \text{I}^-$ is effectively maintained in all reacting systems. It follows that the net rate of reaction is given by

$$-\frac{d[\Sigma\text{I}_2]}{dt} = k_5[\text{NO}_2]^2 = \frac{k_1[\text{NO}_2^-][\text{I}_2]}{\frac{k_2k_4}{k_3k_5} \frac{[\text{I}^-]^2}{[\text{NO}_2^-]} + 1} \quad (5)$$

$$\text{or} \quad -\frac{d[\Sigma\text{I}_2]}{dt} = \frac{k_1K_3[\text{NO}_2^-][\Sigma\text{I}_2]}{\{K_3 + [\text{I}^-]\} \left\{ \frac{k_2k_4}{k_3k_5} \frac{[\text{I}^-]^2}{[\text{NO}_2^-]} + 1 \right\}} \quad (5a)$$

in formal agreement with the empirical equation (2).

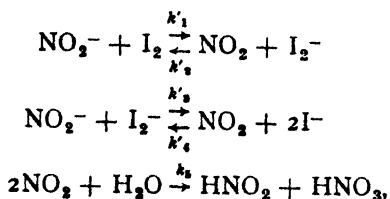
Mechanism II., with the corresponding assumptions with regard to the relative rates of the part-processes, leads to an equation identical with (5a), as does also an alternative form of Mechanism II., *viz.*,



We have, however, definite evidence (*vide infra*) in support of the view that iodine atoms participate in the reaction, and therefore we need not discuss Mechanism II. or its variants further.

Reverting to Mechanism I., it may be noted that addition to it of the

rapidly maintained equilibrium $\text{I} + \text{I}^- \rightleftharpoons \text{I}_2^-$ still leads to an equation formally identical with (5a), and, in fact the mechanism Ia



which is a simple variant of Mechanism I., yields equation (5a) with the constants k'_1 , k'_2 , k'_3 and k'_4 substituted for k_1 , k_2 , k_3 and k_4 respectively. According to Griffith, McKeown and Winn,⁶ the equilibrium constant

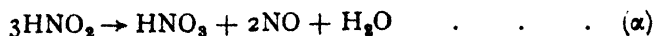
$K_4 = \frac{[\text{I}][\text{I}^-]}{[\text{I}_2^-]}$ is at most 10^{-4} , and hence, even at the lowest concentrations of iodide here employed, the concentration of I_2^- exceeds that of I atoms. Mechanism Ia may therefore be somewhat more likely than Mechanism I., but as there appears to be no means of distinguishing between them, we may confine our further discussion to Mechanism I. itself.

Identifying k_1K_3 and $\frac{k_2k_4}{k_3k_5}$ of equation (5a) with the constants k and A respectively of equation (2), we obtain for the ratio $\frac{k_2k_4}{k_3k_5}$ the values 157 at 50° and 143 at 60° . The values of k_1 under the various conditions studied are given in the last column of Table II. These values refer to the reaction in media containing sodium salts. The values of k_1 and $\frac{k_2k_4}{k_3k_5}$ in presence of potassium salts at $\mu = 1.34$ and 60° are 0.438 and 176 respectively. The temperature coefficients of k_1 in the intervals $40^\circ - 50^\circ$ and $50^\circ - 60^\circ$ are 3.86 and 3.54 respectively, corresponding to a critical increment E_1 of 27,000 cal. The ratio $\frac{k_2k_4}{k_3k_5}$ definitely decreases with increasing temperature, but its dependence on temperature is relatively small. It corresponds to a "critical increment" E_A of — 2000 cal.

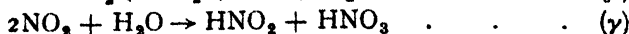
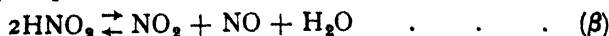
Discussion.

Apart from the fact that Mechanism I. for the reaction between nitrite and iodine predicts the correct kinetic law, two independent tests of its validity are available. The first of these concerns the assumed intermediacy of NO_2 , the second the rôle of iodine atoms in the reaction. We shall deal with these tests in order.

The mechanism of decomposition of nitrous acid in aqueous solution, which has been the subject of many investigations in the past, has been finally elucidated by the careful studies of Abel and his co-workers.⁶ It has been found that the net reaction



is composite of the part-processes



⁶ Griffith, McKeown and Winn, *Trans. Faraday Soc.*, 1933, **29**, 386.

of which (β) is a rapidly maintained equilibrium, while (γ) determines the measured rate of decomposition of the nitrous acid.* Now reaction (γ) has also been assumed to be the rate-determining step in our mechanism for the oxidation of nitrite by iodine, and accordingly it should be possible to correlate quantitatively our kinetic measurements of this reaction with those of Abel for the decomposition of nitrous acid. This may be done as follows.

Reaction (α) is found by Abel to follow the kinetic law

$$-\frac{d[\text{HNO}_2]}{dt} = k_\alpha \frac{[\text{HNO}_2]^4}{p_{\text{NO}}^2} \quad (6)$$

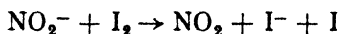
But from Abel's mechanism this rate is also given by

$$-\frac{d[\text{HNO}_2]}{dt} = -\frac{3}{2} \frac{d[\text{NO}_2]}{dt} = 3k_5[\text{NO}_2]^2 \quad (7)$$

where k_5 is the velocity coefficient of process (γ). Hence

$$k_5 = \frac{1}{3} k_\alpha \frac{[\text{HNO}_2]^4}{p_{\text{NO}}^2 [\text{NO}_2]^2} = \frac{1}{3} k_\alpha \frac{K_\beta^2}{D^2} \quad (8)$$

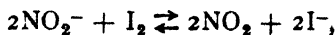
where $K_\beta = \frac{[\text{HNO}_2]^2}{p_{\text{NO}} p_{\text{NO}_2}}$ is the equilibrium constant of process (β) and $D = \frac{[\text{NO}_2]}{p_{\text{NO}_2}}$ is the solubility coefficient of NO_2 in water. On the other hand, the constants which we have evaluated from the nitrite-iodine reaction are the velocity constant k_1 of the primary process



and the ratio $\frac{k_2 k_4}{k_3 k_5} = A$ of the velocity constants of the other part-processes in Mechanism I. In terms of these we have

$$k_5 = \frac{k_1 (k_2 k_4)}{A (k_1 k_3)} \quad (9)$$

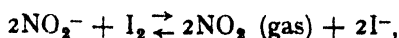
But the factor $\frac{k_2 k_4}{k_1 k_3}$ is simply the equilibrium constant of the reaction



which is compounded of the k_1 , k_2 , k_3 , and k_4 reactions, or

$$\frac{k_2 k_4}{k_1 k_3} = \frac{K}{D^2} \quad (10)$$

where K is the equilibrium constant of the reaction



i.e.,

$$K = \frac{[\text{NO}_2^-]^2 [\text{I}_2]}{p_{\text{NO}_2}^2 [\text{I}^-]^2}.$$

Combining (9) and (10), we obtain

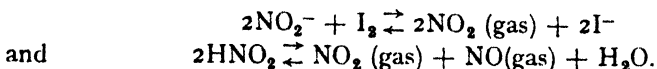
$$k_5 = \frac{k_1}{A} \cdot \frac{K}{D^2} \quad (11)$$

* Abel writes (β) and (γ) in terms of N_2O_4 , instead of NO_2 , a formal difference which naturally does not affect the argument.

and comparing (8) and (11) the following relation results between Abel's constant k_α and our constants k_1 and A :—

$$k_\alpha = \frac{3k_1}{A} \cdot \frac{K}{K_\beta^2} \quad (12)$$

It should thus be possible to evaluate Abel's k_α at say 60° C. from our own velocity constants and the equilibrium constants K and K_β of the reactions



These equilibrium constants have been evaluated from the free energies of the participants at 25° and the heats of reaction, using the data from International Critical Tables. They are:

$$\begin{aligned} K(25^\circ) &= 6.9 \times 10^9; & K_\beta(25^\circ) &= 1.44 \times 10^2 \\ Q_p &= 33,800 \text{ cal.}; & Q_p &= 18,350 \text{ cal.} \\ K(60^\circ) &= 1.5 \times 10^7; & K_\beta(60^\circ) &= 5.54. \end{aligned}$$

Using equation (4) to correct our k_1 of Table II. to zero ionic strength, we obtain $k_1(\mu=0) = 0.568$ and $A = 143$ at 60°. Hence k_α at $\mu=0$ and 60° is calculated from equation (12) to be 5825, whereas Abel's experimental value is 5130. In view of the inevitable uncertainties in the values of K and K_β the agreement is very satisfactory, and it must be regarded as strong evidence for the hypothesis that NO_2 participates in the nitrite-iodine reaction in such a manner as to make the rate-determining process $2\text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{HNO}_2 + \text{HNO}_3$.

As a further test of equation (12), the critical increment of k_α may also be calculated from the temperature dependence of k_1 , A , K , and K_β . We have

$$\begin{aligned} E_\alpha &= E_1 - E_A - Q_K + 2Q_{K_\beta} \quad (13) \\ &= 27,000 + 2000 - 33,800 + 36,700 \\ &= 31,900 \text{ cal.} \end{aligned}$$

This lies about 3000 cal. above Abel's value for E_α of 28,600 cal. Probably this difference simply represents an accumulation of errors in the various terms involved.

Turning to the consideration of the rôle of iodine atoms in the nitrite-iodine reaction, it should at once be remarked that the deduction of equation (5) from Mechanism I. involves two major assumptions, one of which has hitherto not been explicitly stated. It has been assumed that the k_3 and k_4 reactions are always fast compared with the other processes in the mechanism, but it has also been implicitly assumed that these same reactions are fast compared with any such processes as $\text{I}_2 \rightleftharpoons 2\text{I}$ or $\text{I}_3^- + \text{I}^- \rightleftharpoons 2\text{I}_2^-$ (coupled with $\text{I}_2 \rightleftharpoons \text{I}^- + \text{I}$) which, in the absence of nitrite, would maintain a thermal equilibrium concentration of iodine atoms $[\text{I}]$, in the system. In effect, we have postulated that the instantaneous concentration of iodine atoms is controlled solely by the

equilibrium $\text{NO}_2^- + \text{I} \xrightleftharpoons[k_4]{k_3} \text{NO}_2 + \text{I}^-$, and that the observed rate of reaction, viz., $k_5[\text{NO}_2]^{1/2}$, represents the lack of balance between the k_1 and k_3 reactions. Without the progressive drain on the NO_2 by the k_5 reaction, the k_1 and k_3 reactions would also balance, and the $\text{NO}_2 \rightleftharpoons \text{NO}_2^-$

couple would simply act as a catalyst for the production and disappearance of iodine atoms. Under these circumstances, however, the concentration of iodine atoms must assume its thermal equilibrium value $[I]_e$, and therefore

$$\frac{[NO_2]_e[I^-][I]_e}{[NO_2^-][I_2]} = \frac{k_1}{k_2} \quad (14)$$

and

$$\frac{[NO_2]_e[I^-]}{[NO_2^-][I]_e} = \frac{k_3}{k_4} \quad (15)$$

where $[NO_2]_e$ is the stationary concentration of NO_2 under these ideal conditions. The velocity constants k_1 , k_2 , k_3 and k_4 must therefore be such that

$$\frac{[I]_e^2}{[I_2]} = \frac{k_1 k_4}{k_2 k_3} \quad (16)$$

The actual occurrence of the k_5 reaction upsets this balance and has the effect of reducing the concentrations of NO_2 and I atoms below their equilibrium values. We now have

$$\frac{[NO_2][I^-]}{[NO_2^-][I]} = \frac{k_3}{k_4} \quad (17)$$

and

$$k_1[NO_2^-][I_2] - k_2[NO_2][I^-][I] = k_5[NO_2]^2 \quad (18)$$

from which, it may be noted, equation (5) directly follows. Combining equations (17) and (18) with (16), it also follows that the ratio (F) of $[I]$ to $[I]_e$ is given by

$$F = \frac{[I]}{[I]_e} = \sqrt{\frac{A[I^-]^2/[NO_2^-]}{A[I^-]^2/[NO_2^-] + 1}} \quad (19)$$

where $A = \frac{k_2 k_4}{k_3 k_5}$ as heretofore. Examination of equation (19) shows that $[I]$ should approximate to $[I]_e$ for high values of $[I^-]^2/[NO_2^-]$, that is for an observed slow rate of reaction between nitrite and iodine, whereas for low values of $[I^-]^2/[NO_2^-]$, that is, for a high rate of reaction, the concentration of iodine atoms should be maintained considerably less than its thermal equilibrium value.

Now we have previously demonstrated,³ and the result has been confirmed by other workers,^{2, 4} that the thermal reaction between iodine and an oxalate is composite of two simultaneous processes, the one unimolecular, the other semi-molecular with respect to iodine. The first of these is interpreted as a reaction between $HC_2O_4^-$ ions and HIO , the other as a reaction between $C_2O_4^{--}$ ions and iodine atoms. If iodine atoms participate also in the nitrite-iodine reaction as above described, it follows on the basis of the above analysis that in a reaction mixture containing nitrite, oxalate, and iodine, the iodine should be consumed at a rate less than that computed as the additive effect of the separate reactions of iodine with oxalate and with nitrite. We have carried out experiments to test this; the predicted decrease in the rate of consumption of iodine is confirmed, and furthermore the results may be quantitatively interpreted on the basis of equation (19).

Solutions of oxalates, in which the oxalate ion present is predominantly $C_2O_4^{--}$, react with I_2 according to the equation³

$$-\frac{d[\Sigma I_2]}{dt} = [C_2O_4^{--}] \left\{ \frac{\sqrt{[\Sigma I_2]}}{\sqrt{K_3} + [I^-]} + k_1'' \frac{[\Sigma I_2]}{[I^-]\{K_3 + [I^-]\}} \right\} \quad (20)$$

where the first term inside the brackets refers to the semi-molecular process and the second to the unimolecular process. Hence it follows that in solutions containing both nitrite and oxalate the rate of consumption of iodine should be given by

$$-\frac{d[\Sigma I_2]}{dt} = [C_2O_4^{--}] \left\{ k_1 F \frac{\sqrt{[\Sigma I_2]}}{\sqrt{K_3 + [I^-]}} + k_1'' \frac{[\Sigma I_2]}{[I^-] \{K_3 + [I^-]\}} \right\} + k' \frac{[NO_2^-][\Sigma I_2]}{K_3 + [I^-]} \quad (21)$$

where F is defined by equation (19). From separate experiments in absence of nitrite, carried out at 50° and $\mu=0.95$, we find $k_1''=38.0 \times 10^{-8}$ and $k_1=48.2 \times 10^{-6}$. Using these values of k_1'' and k_1 and the pertinent values of k' for the nitrite-iodine reaction, we have employed equation (21) to calculate the rates of disappearance of iodine in solutions containing both oxalate and nitrite, and have compared these rates with those found experimentally. As equation (21) is non-integrable, we have used the method of finite differences, and have calculated values of $\Delta[\Sigma I_2]_{tot.}$, gram-molecules of I_2 transformed per litre, in time intervals Δt from the equation

$$\Delta[\Sigma I_2]_{tot.} = \Delta t \left[[C_2O_4^{--}] \left\{ k_1 F \frac{\sqrt{[\Sigma I_2]_m}}{\sqrt{K_3 + [I^-]_m}} \right. \right. \\ \text{I.} \\ \left. \left. + k_1'' \frac{[\Sigma I_2]_m}{[I^-]_m \{K_3 + [I^-]_m\}} \right\} + k' \frac{[NO_2^-][\Sigma I_2]_m}{K_3 + [I^-]_m} \right] \quad (21a) \\ \text{II.} \qquad \qquad \qquad \text{III.}$$

where $[\Sigma I_2]_m$ and $[I^-]_m$ are the mean values of the concentrations of titratable iodine and of iodide over the relevant time interval, and I, II, and III are the separate contributions of the three terms on the right-hand side of the equation to the total $\Delta[\Sigma I_2]$.

Table VI. reproduces the results of one such experiment and the calculations based thereon.

The last column in the upper half of the table gives the observed amounts of iodine disappeared, and the last two columns in the lower half give the calculated values:

(a) With the assumption that the oxalate-iodine and nitrite-iodine reactions are additive, that is, making $F = 1$ in equation (21a);

(b) Using equation (21a) with the values of F given in the table and based on equation (19).

It will be seen that the values calculated by method (b) are in good agreement with the experimentally observed values, whereas method (a) gives values considerably too high. We have carried out five such test experiments in all. Space will not permit of reproducing the results of these in detail, but their main features may be summarised as follows. In them the value of F has been varied from 0.15 to 0.95. Calculation by method (a) yields consistently high values for $\Delta[\Sigma I_2]_{tot.}$, deviations up to 35 per cent. being obtained. Calculating by method (b), two of the experiments give values of $\Delta[\Sigma I_2]_{tot.}$ (calc.) slightly higher than the observed values; in the remaining three experiments (of which the experiment of Table VI. is one) the reverse is true. In no case, however, is any single value of $\Delta[\Sigma I_2]_{tot.}$ calculated by method (b) more than 5 per cent. different from the observed value. The results of these five

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TABLE VI.— $[\text{NaNO}_2] = 0.1807$; $[\text{NaKC}_2\text{O}_4] = \frac{1}{2}$; $[\text{Na}_2\text{HPO}_4] = 0.05$; $[\text{KH}_2\text{PO}_4] = 0.1$; $[\text{KI}]_0 = 0.01$; $[\Sigma\text{I}]_0 = 0.002$ APPROX.; TEMP. = 50° ; $\mu = 0.94$.

$[\Sigma\text{I}_2] \times 10^3$	Δt (min.)	$[\Sigma\text{I}_2]_{\text{m}} \times 10^3$	$\{K_3 + [\text{I}^-]_{\text{m}}\} \times 10^3$	F.	$\Delta[\Sigma\text{I}_2]_{\text{tot.}}$ $\times 10^4$ (obsd.).
1.915	23.15	1.807	1.111	0.251	2.16
1.699	34.58	1.566	1.177	0.268	2.65
1.434	46.30	1.297	1.251	0.287	2.74
1.160	59.15	1.027	1.326	0.306	2.65
0.895	82.63	0.7613	1.401	0.325	2.67
0.628					

Δt	$\Delta[\Sigma\text{I}_2]_{\text{I}} \times 10^3$	$\Delta[\Sigma\text{I}_2]_{\text{II}} \times 10^3$	$\Delta[\Sigma\text{I}_2]_{\text{III}} \times 10^3$	$\Delta[\Sigma\text{I}_2]_{\text{tot.}} \times 10^4$	
				Calc. (a).	Calc. (b).
23.15	1.88	2.69	16.33	2.652	2.090
34.58	2.71	3.06	19.78	3.297	2.555
46.30	3.44	2.96	20.41	3.535	2.681
59.15	4.05	2.64	19.23	3.510	2.592
82.63	5.03	2.42	18.62	3.652	2.607

experiments are thus entirely consistent with equation (19), and therefore with the theory that iodine atoms participate in the nitrite-iodine reaction.

Finally, it is to be noted that of the velocity constants, k_1 , k_2 , k_3 , k_4 and k_5 of our mechanism, only k_1 is at present determinable. The others, or more precisely k_3 , k_5 and the ratio k_3/k_4 , could be calculated from existing data if a knowledge of the solubility coefficients of NO_2 and of monatomic iodine in water were available. As this is not the case, we may for the present refrain from speculating on these matters. It is hoped, however, that the *photochemical* reaction between nitrite and iodine, which we are now re-investigating, may shed further light on the reaction mechanism.

Summary.

The kinetics of the nitrite-iodine reaction have been investigated in phosphate buffers at temperatures of 40° , 50° and 60° . The reaction rate is given by

$$-\frac{d[\Sigma\text{I}_2]}{dt} = k \frac{[\text{NO}_2^-][\Sigma\text{I}_2]}{\{K_3 + [\text{I}^-]\} \left\{ A \frac{[\text{I}^-]^2}{[\text{NO}_2^-]} + 1 \right\}},$$

where k and A are constants and K_3 is the tri-iodide equilibrium constant. k and A have been evaluated at different temperatures and for different neutral salt environments. This kinetic equation has been interpreted in terms of a reaction mechanism involving NO_2 and iodine atoms as intermediaries. The presumed rôle of NO_2 is substantiated by comparison of

our kinetic data with those of Abel and co-workers for the decomposition of free nitrous acid, while independent confirmation of the rôle of iodine atoms in the reaction has been obtained by use of the iodine-oxalate reaction as an "indicator reaction" for iodine atoms.

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MEAN VALUES FOR THE DIPOLE MOMENTS OF THE HARMONIC AND ANHARMONIC OSCILLATOR IN QUANTUM MECHANICS.

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In a previous paper,¹ one of the authors has calculated the mean dipole moment of a classical harmonic oscillator, and shown that for polarisable ions the mean moment is a function of the amplitude. This result was then applied to calculate the difference in the mean dipole moments of isotopic molecules arising from the difference in the amplitudes of the zero point vibrations. Such a procedure is open to criticism, since zero point energy is essentially a quantum mechanical phenomenon, and cannot be legitimately treated as a classical vibration. In particular, the eigenfunction of the lowest state of a harmonic oscillator shows that the configuration of maximum probability corresponds to the position of equilibrium, while in a classical oscillator the particle is most likely to be found at the extremes of its motion.² The present paper gives a quantum mechanical calculation of the mean values involved, and extends the treatment to higher vibrational states and (to a first approximation) to an anharmonic oscillator.

The variation of the instantaneous dipole moment with the inter-nuclear distance depends on the electronic distribution and cannot be represented accurately by any general theoretical or empirical equation. The electrical state of a diatomic molecule can, however, be represented at least approximately by a model consisting of polarisable ions. In the present paper we shall consider only the case in which only one of the ions is polarisable, corresponding to a diatomic molecule or group in which one of the atoms is hydrogen (or deuterium). The instantaneous dipole moment is then given by

$$\mu = e(a + x) - \frac{\alpha e}{(a + x)^2} \cdot \cdot \cdot \cdot (1)$$

¹ R. P. Bell, *Trans. Faraday Soc.*, 1935, **31**, 1345.

² The same criticism applies in principle to any quantitative treatment of zero point energy as a classical vibration, e.g. in dealing with the minimum distance of approach of isotopic molecules (cf. R. P. Bell and J. H. Wolfenden, *J. Chem. Soc.*, 1935, 823; A. R. Ubbelohde, *Trans. Faraday Soc.*, 1936, **32**, 525), though the results of the present paper show that the errors involved in a classical treatment will in most cases be small.

and the moment in the equilibrium position by

$$\mu_0 = ea - \frac{e\alpha}{a^2}, \quad (2)$$

where a is the equilibrium distance between ions of charges $+e$ and $-e$, x is the displacement from the equilibrium position, and α the polarisability of one of the ions.

It is convenient to introduce a new variable ξ defined by $x = b\xi$, where $b = (\hbar/4\pi^2 m\nu)^{\frac{1}{2}}$ is the amplitude of a classical harmonic oscillation of energy $\frac{1}{2}\hbar\nu$, m being the reduced mass and ν the frequency. The expression for μ can then be expanded in powers of ξ , giving

$$\frac{\mu}{ea} = \frac{a + b\xi}{a} - \frac{\alpha}{a(a + b\xi)^2} \\ = \frac{\mu_0}{ea} + \xi \frac{b}{a} \left(1 + \frac{2\alpha}{a^3} \right) - \xi^2 3 \frac{b^2}{a^2} \frac{\alpha}{a^3} + \xi^3 4 \frac{b^3}{a^3} \frac{\alpha}{a^3} - \xi^4 5 \frac{b^4}{a^4} \frac{\alpha}{a^3} + O(\xi^5). \quad (3)$$

Since in practice $b/a < 1/10$, it is necessary to retain only the first few terms of the expansion. The mean value of μ is then obtained by inserting the mean values of ξ , ξ^2 , etc., in equation (3). Any empirical or theoretical expression for μ which is more accurate than equation (1) can be treated in the same way by expanding in powers of ξ .

The mean value of ξ^r in the n th vibrational state is given by

$$\bar{\xi}^r = \int_{-\infty}^{+\infty} \psi_n^2 \xi^r dx = b \int_{-\infty}^{+\infty} \psi_n^2 \xi^r d\xi, \quad (4)$$

where ψ_n is the normalised wave function. ψ_n has the well-known form

$$\psi_n = \left\{ \frac{1}{2^n n! b \pi^{\frac{1}{2}}} \right\}^{\frac{1}{2}} e^{-\xi^2/2} H_n(\xi) \quad (5)$$

where $H_n(\xi)$ is the n th Hermitean polynomial. For present purposes these polynomials are most conveniently defined by means of the generating function

$$S(\xi, s) = e^{\xi^2 - (s - \xi)^2} = \sum_n \frac{H_n(\xi)}{n!} s^n. \quad (6)$$

The integrals in equation (4) are evaluated by taking a second generating function

$$T(\xi, t) = e^{\xi^2 - (t - \xi)^2} = \sum_k \frac{H_k(\xi)}{k!} t^k,$$

and considering the product

$$\int_{-\infty}^{+\infty} S T e^{-\xi^2} \xi^r d\xi = e^{2st} \int_{-\infty}^{+\infty} e^{-(\xi - s - t)^2} \xi^r d\xi \\ = e^{2st} \int_{-\infty}^{+\infty} e^{-\xi^2} (\xi + s + t)^2 d\xi = \sum_n \sum_k \frac{s^n t^k}{n! k!} \int_{-\infty}^{+\infty} H_n H_k e^{-\xi^2} \xi^r d\xi. \quad (7)$$

The value of $\int_{-\infty}^{+\infty} H_n H_k e^{-\xi^2} \xi^r d\xi$ is obtained by expanding e^{2st} and equating coefficients of $s^n t^k$ in the last two expressions in equation (7). Only integrals with $n = k$ are required in equation (4).

The following results are obtained

$$\overline{\xi_n^r} = 0 \quad \text{if } r \text{ is odd,} \quad (8)$$

$$\overline{\xi_n^2} = n + \frac{1}{2}, \quad \overline{\xi_n^4} = \frac{3}{2}(n^2 + n + \frac{1}{2}).$$

Inserting these values in equation (3)

$$\frac{\bar{\mu} - \mu_0}{ea} = -\frac{\alpha}{a^3} \left\{ 3(n + \frac{1}{2}) \frac{b^2}{a^2} + \frac{15}{2}(n^2 + n + \frac{1}{2}) \frac{b^4}{a^4} + O \left(\frac{b^6}{a^6} \right) \right\}. \quad (9)$$

For the particular case of a molecule in its lowest vibrational state (as is actually the case at ordinary temperatures)

$$\frac{\bar{\mu} - \mu_0}{ea} = -\frac{\alpha}{a^3} \left\{ \frac{3}{2} \frac{b^2}{a^2} + \frac{15}{4} \frac{b^4}{a^4} + O \left(\frac{b^6}{a^6} \right) \right\}. \quad (10)$$

Equation (9) can be used to estimate the change of $\bar{\mu}$ at high temperatures due to an increase in the vibrational quantum number, and equation (10) to estimate the dependence of $\bar{\mu}$ upon b and hence upon the mass of the atoms (isotope effect). In both cases the effect would be absent for a dipole consisting of non-polarisable ions ($\alpha = 0$).

For a classical harmonic oscillator having the same energy, ξ is given by

$$\xi_n = \sqrt{2n+1} \sin 2\pi\nu t, \quad (11)$$

and the mean values of ξ^2 and ξ^4 become

$$\begin{aligned} \overline{\xi_n^2} &= (2n+1) \overline{\sin^2 \theta} = n + \frac{1}{2} \\ \overline{\xi_n^4} &= (2n+1)^2 \overline{\sin^4 \theta} = \frac{3}{2}(n^2 + n + \frac{1}{2}). \end{aligned} \quad (12)$$

Comparison with equation (8) shows that the classical and quantum mechanical treatments give identical values for $\overline{\xi_n^2}$, but different values for $\overline{\xi_n^4}$ (and for higher powers of ξ^2); hence the classical treatment gives the value for $\bar{\mu}$ correct to terms in b^2/a^2 . As would be expected, the divergence between the two sets of results becomes relatively smaller as n increases.

For practical purposes the value of $\overline{\mu^2}$ is much more important than that of $\bar{\mu}$: for instance, the experimental measurement of dipole moments always gives the root mean square moment and not the mean moment. From equation (3)

$$\begin{aligned} \frac{\mu^2}{e^2 a^2} &= \frac{(a + b\xi)^2}{a^2} - \frac{2\alpha}{a^3(a + b\xi)} + \frac{\alpha^2}{a^2(a + b\xi)^4} \\ &= \frac{\mu_0^2}{e^2 a^2} + \xi \frac{b}{a} \left(2 + \frac{2\alpha}{a^3} - \frac{4\alpha^2}{a^6} \right) + \xi^2 \frac{b^2}{a^2} \left(1 - \frac{2\alpha}{a^3} + \frac{10\alpha^2}{a^6} \right) \\ &\quad + \xi^3 \frac{b^3}{a^3} \left(\frac{2\alpha}{a^3} - \frac{20\alpha^2}{a^6} \right) - \xi^4 \frac{b^4}{a^4} \left(\frac{2\alpha}{a^3} - \frac{35\alpha^2}{a^6} \right) + O(\xi^5). \end{aligned} \quad (13)$$

Inserting the mean values from equation (8),

$$\begin{aligned} \frac{\overline{\mu^2} - \mu_0^2}{e^2 a^2} &= (n + \frac{1}{2}) \frac{b^2}{a^2} \left(1 - \frac{2\alpha}{a^3} + \frac{10\alpha^2}{a^6} \right) \\ &\quad - \frac{3}{2}(n^2 + n + \frac{1}{2}) \frac{b^4}{a^4} \left(\frac{2\alpha}{a^3} - \frac{35\alpha^2}{a^6} \right) + O \left(\frac{b^6}{a^6} \right). \end{aligned} \quad (14)$$

and for the lowest vibrational state,

$$\frac{\bar{\mu}^2 - \mu_0^2}{e^2 a^2} = \frac{1}{2} \frac{b^2}{a^2} \left(1 - \frac{2\alpha}{a^3} + \frac{10\alpha^2}{a^6} \right) - \frac{3}{4} \frac{b^4}{a^4} \left(\frac{2\alpha}{a^3} - \frac{35\alpha^2}{a^6} \right) + O \left(\frac{b^6}{a^6} \right). \quad (15)$$

Equations (14) and (15) show that even for a dipole composed of non-polarisable ions the observed moment (unlike $\bar{\mu}$) will depend upon the vibrational level and upon the mass of the particles. Further, the expression $\left(1 - \frac{2\alpha}{a^3} + \frac{10\alpha^2}{a^6} \right)$ (which is the only coefficient of importance in practice) is always positive, so that the observed moment will always increase with increasing vibrational quantum number, and will be greater for a hydrogen compound than for the corresponding deuterium compound. (The opposite conclusions are reached by considering $\bar{\mu}$: cf. equations (9) and (10).)

As an example we shall apply our formulæ to the HCl and DCl molecules, although they are not strictly applicable to this case. Our formulæ are derived for a molecule in which the vibrating particles are ions. If, on the other hand, the vibrational quantum number of the HCl molecule is steadily increased without altering the electronic quantum number, the molecule gradually dissociates into two neutral atoms, not into two ions. However, we believe that the inaccuracy of our model may be partly compensated by taking as the value of the polarisability of Cl^- not the true value but the value calculated from equation (2) and the experimental value³ for μ . For HCl we have then

$$a = 1.23 \times 10^{-8}, \quad b = 1.08 \times 10^{-9}, \quad (\bar{\mu}^2)^{\frac{1}{2}} = 1.03 \times 10^{-18} \text{ (at ordinary temperatures)}, \quad \alpha = 1.70 \times 10^{-24}.$$

$(\bar{\mu}^2)^{\frac{1}{2}}$ for DCl is found to be 0.91×10^{-18} , a difference which should be easily detected experimentally. (The only measurements with deuterium compounds so far reported deal with D_2O and ND_3 , both of which are found to have a moment slightly *greater* than the corresponding hydrogen compounds. However, both these molecules are bent, and the effect is probably due to a change in the angle between the bonds.) It is similarly found that for HCl molecules in the first excited vibrational level ($n = 1$) $(\bar{\mu}^2)^{\frac{1}{2}} = 1.62 \times 10^{-18}$. There should thus be a considerable increase in the observed moment at sufficiently high temperatures, though it would hardly be observable at temperatures below about 1000° . Quite apart from the validity of any particular model, data for simple linear molecules such as HCl and DCl would give valuable information about the variation of electron distribution with internuclear distance.

The same treatment can easily be extended to obtain a first approximation for a slightly anharmonic oscillator. If the potential energy of the oscillator is given by

$$V = 2\pi^2 m \nu^2 x^2 - \beta x^3 \quad . \quad . \quad . \quad (16)$$

then the first order wave function for the n th vibrational state is

$$\psi'_n = \psi_n + \beta \sum_{k=0}^{\infty} \frac{\int_{-\infty}^{+\infty} \psi_n \psi_k x^3 dx}{W_n - W_k} \psi_k, \quad . \quad . \quad (17)$$

³ Cf. Debye, *Polare Molekeln*, p. 73, Leipzig, 1929.

where ψ_n, W_n are the wave function and the energy when $\beta = 0$. Putting $W_n = (n + \frac{1}{2})h\nu$, and using equation (7) to evaluate the integrals, this gives

$$\psi'_n = \psi_n + \frac{\beta h^{\frac{1}{2}}}{8\pi^3 m^{\frac{3}{2}} \nu^{\frac{5}{2}}} \{3(n+1)^{\frac{3}{2}} \psi_{n+1} - 3n^{\frac{3}{2}} \psi_{n-1} + \frac{1}{3} \sqrt{(n+1)(n+2)(n+3)} \psi_{n+3} - \frac{1}{3} \sqrt{n(n-1)(n-2)} \psi_{n-3}\} \quad (18)$$

The mean values of $\xi', \xi'',$ etc., are then calculated by inserting this wave function in equation (4), again using equation (7). The results of somewhat laborious calculations are as follows:—

$$\left. \begin{aligned} \bar{\xi}' &= \frac{3\beta h^{\frac{1}{2}}}{16\pi^3 m^{\frac{3}{2}} \nu^{\frac{5}{2}}} (2n+1) \\ \bar{\xi}'' &= (n + \frac{1}{2}) + \frac{\beta^2 h}{9216\pi^6 m^3 \nu^5} \{238n^4 + 404n^3 + 1415n^2 + 1231n + 339\} \\ \bar{\xi}''' &= \frac{\beta h^{\frac{1}{2}}}{32\pi^3 m^{\frac{3}{2}} \nu^{\frac{5}{2}}} \{30n^2 + 30n + 11\} \\ \bar{\xi}'''' &= \frac{1}{2}(n^2 + n + \frac{1}{2}) + \frac{\beta^2 h}{6144\pi^6 m^3 \nu^5} \{172n^5 + 430n^4 + 3462n^3 + 5432n^2 + 4030n + 1059\} \end{aligned} \right\} \quad (19)$$

The corresponding values of $\bar{\mu}$ and $\bar{\mu}^2$ are obtained by inserting these mean values in equations (3) and (13). Since for an actual molecule β is positive, the anharmonic terms increase the effects described above.

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A NOTE ON EVAPORATION FROM IRREGULAR SURFACES.

By H. W. MELVILLE.

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In making use of the Herz-Knudsen effusion equation to determine the vapour pressure of a substance by sublimation in a vacuum two simplifying assumptions are made, (a) the condensation coefficient of molecules on the surface from which they are evaporating is unity, and (b) the effective area of the surface, if irregular, is equal to its projected geometrical area. It might be imagined, however, that if the surface from which evaporation is taking place is made extremely rough, then the rate of evaporation would be increased in proportion to the increase in surface area, much in the same way as the catalytic activity of a material is believed to be considerably increased by breaking up its surface by successive oxidations and reductions. In point of fact the increase in rate of evaporation on roughening a surface has been suggested as a means of finding the true area of the surface.¹

¹ Cf. Rideal, *Surface Chemistry*, p. 177.

1. The amount which escapes is $2\alpha A$ and therefore the amount which hits the opposite wall is $2\alpha A(\operatorname{cosec} \theta - 1)$, of these only β condense. The remainder $(1 - \beta) 2\alpha A(\operatorname{cosec} \theta - 1)$ evaporate.

2. Of these a fraction $\sin \theta$ escape, *i.e.*, $\frac{(1 - \beta) 2\alpha A(\operatorname{cosec} \theta - 1) \sin \theta}{(1 - \sin \theta)}$ hits the opposite wall, *i.e.*,

$$(1 - \beta) 2\alpha A (\operatorname{cosec} \theta - 1) (1 - \sin \theta);$$

of these β condense. The remainder

$$(1 - \beta)^2 2\alpha A (\operatorname{cosec} \theta - 1) (1 - \sin \theta) \times \sin \theta$$

evaporate.

3. Of these a fraction $\sin \theta$ escapes, *i.e.*,

$$\frac{(1 - \beta)^2 2\alpha A (\operatorname{cosec} \theta - 1) (1 - \sin \theta) \times \sin^2 \theta}{(1 - \sin \theta)}$$

of these a fraction $(1 - \sin \theta)$ hits the opposite wall, *i.e.*,

$$(1 - \beta)^2 2\alpha A (\operatorname{cosec} \theta - 1) (1 - \sin \theta)^2 (\sin^2 \theta)$$

of these β condense. The remainder

$$(1 - \beta)^3 2\alpha A (\operatorname{cosec} \theta - 1) (1 - \sin \theta)^2 \sin^2 \theta$$

evaporate.

4. Of these a fraction $\sin \theta$ escape, *i.e.*,

$$\frac{(1 - \beta)^3 2\alpha A (\operatorname{cosec} \theta - 1) (1 - \sin \theta)^2 \sin^3 \theta}{(1 - \sin \theta)}$$

For the n th evaporation

$$\frac{(1 - \beta)^{n-1} 2\alpha A (\operatorname{cosec} \theta - 1) (1 - \sin \theta)^{n-2} \sin^{n-1} \theta}{(1 - \sin \theta)}$$

escape.

$1 - \beta$, $\sin \theta$ and $(1 - \sin \theta)$ are all less than unity and hence the sum of the terms of the series converges to a finite magnitude. Its value is

$$2\alpha A \left\{ 1 + (1 - \beta) (\operatorname{cosec} \theta - 1) \sin \theta + \frac{(1 - \beta)^2 (\operatorname{cosec} \theta - 1) \sin^2 \theta (1 - \sin \theta)}{1 - (1 - \beta) \sin \theta (\operatorname{cosec} \theta - 1) (1 - \sin \theta)} \right\}$$

The factor within the bracket has been evaluated for a number of different values of α and of θ and the results are shown in Fig. 2. In the first place

it will be seen that the limits for $\theta = 0$ and for $\theta = 90$ are unity. Even with the small condensation coefficient of 0.1 and assuming random distribution of crack angles, the vapour pressure is only increased by a factor of 1.3 to 1.4. If, however, the cracks were

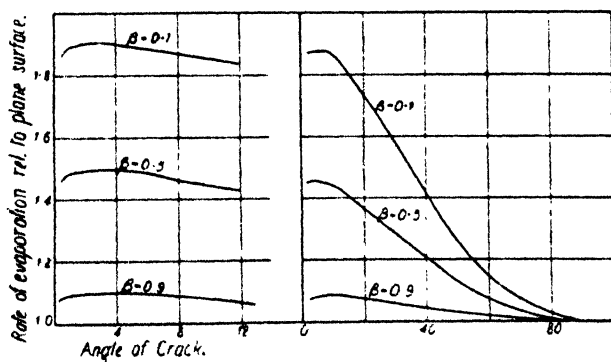


FIG. 2.

numerous and their angles had a tendency to be less than say 5° , then the vapour pressure, on this account, would be erroneous by the

comparatively small factor of two. For phosphorus there is some evidence that the condensation coefficient is not much less than unity at temperatures from -180° to 15° C. The position of the deposit from the plate and also observations on the distribution of the red phosphorus opposite the filaments in the experiments described in the preceding paper show that the P_4 molecule condenses nearly every time it collides with the surface provided this consists of red phosphorus. The conclusion is therefore that the above described effect does not modify the results given in the preceding paper.

Summary.

An investigation has been made of the effect of cracks in a surface on the vapour pressure as determined by molecular distillation. It is shown that if the condensation coefficient is unity there is no increase in the rate of evaporation. If the condensation coefficient is not unity, the rate of evaporation is increased by a relatively small factor, *e.g.*, 1.3 for a condensation coefficient of 0.1.

The author is indebted to Dr. J. K. Roberts for critical discussions on this and on the preceding paper.

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THE EFFECT OF OXYGEN ON THE CLEAN UP OF PHOSPHORUS VAPOUR BY TUNGSTEN FILAMENTS.

BY H. W. MELVILLE AND S. C. GRAY.

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The kinetics of the clean up of phosphorus vapour by hot tungsten filaments have been described in a previous paper.¹ It appears that the mechanism of the reaction is the dissociation of P_4 molecules into P_2 molecules on the tungsten surface, the P_2 molecules then condensing to red phosphorus on diffusing to and striking the walls of the containing vessel. The present paper is concerned (*a*) with the effect of oxygen on the dissociation of P_4 molecules on tungsten, and (*b*) with an attempt to determine the nature of the heterogeneous reaction on tungsten which initiates chains in $P_4 - O_2$ mixtures.²

These latter experiments were mainly concerned at that time with establishing the essential features of this type of heterogeneous-homogeneous reaction, the heterogeneous part of which is zero order with respect to the phosphorus and oxygen concentrations. It was pointed out, however, that it is not possible for the chain initiator to be atomic oxygen nor an oxide of tungsten on account of the low filament temperature (max. 750° K.). The following possibilities are still open:—

(*a*) The P_4 molecule collides with the tungsten surface, which may or may not have been affected by the addition of oxygen and dissociates

¹ Melville and Gray, *Trans. Faraday Soc.*, 1936, **32**, 271.

² Melville and Ludlam, *Proc. Roy. Soc., A*, 1932, **135**, 315.

into two P_2 molecules. These latter react with oxygen thereby starting the chain. The rate of the initiation reaction would therefore be first order with respect to the phosphorus pressure, since the dissociation is also a first-order reaction.

(b) Phosphorus and oxygen are both strongly adsorbed on tungsten, and react together, giving rise to a lower oxide of phosphorus, which evaporates and reacts with the oxygen to initiate the chain. The conditions before evaporation may be regarded diagrammatically as



(c) The tungsten surface is completely covered with a film of oxygen atoms which prevents dissociation of P_4 molecules. The latter, however, are adsorbed on top of the oxygen, and occasionally the P_4O complex evaporates, the empty space being immediately occupied by another oxygen atom. This may be represented as $\text{W}-\text{O}-\text{P}$.

(d) The inverse of (c). Phosphorus is so strongly adsorbed on tungsten that oxygen does not displace it, but is adsorbed on top. The evaporation of a lower oxide again initiates the chain: $\text{W}-\text{P}-\text{O}$.

Experimental.—The apparatus was identical with that used previously, the only addition being an oxygen reservoir. The Pirani gauge was separately calibrated for oxygen.

Results and Discussion.

The first point to be considered is the activity of a deliberately oxidised tungsten filament towards the dissociation of P_4 molecules upon it. In a reaction vessel of 157 c.c., fitted with a filament 0.1 mm. in diameter and effective length 90 mm., the half-life of phosphorus vapour at a pressure of 0.0194 mm. and temperature 635°C . was 3.5 min. On pumping out the phosphorus, admitting oxygen to 0.05 mm. pressure and heating the filament to 830°C ., the oxygen pressure fell to 0.043 mm. The oxygen was pumped out and phosphorus admitted. The clean up could not be measured, there being no detectable pressure change (10^{-4} mm.) in 7 min. The filament had to be heated in vacuo to 1800°C . for 30 min. before the half-life of the phosphorus vapour returned to its previous value — 3.4 min. Heating the filament in 0.04 mm. O_2 for 3 min. at 830° again inhibited the dissociation of the P_4 molecules, the activity being completely restored on heating the filament to 1800° for 40 min. These experiments show immediately that covering the tungsten with a film of adsorbed oxygen atoms³ completely inhibits the dissociation of P_4 molecules, since the cause of inhibition is only removed at temperatures above 1800°C . This constitutes further evidence, in addition to that cited in the previous paper, that the dissociation is a specific chemical reaction.

The next sequence of experiments was carried out to answer the following questions:—

(1) Does the tungsten become appreciably oxidised if heated in oxygen alone to a temperature at which clean up of P_4 is normally measured?

(2) Does the surface of the tungsten become oxidised as a result of the occurrence of the heterogeneous reaction responsible for starting chains in $P_4 - O_2$ mixtures?

(3) Is it possible to dissociate P_4 molecules on an oxygen covered tungsten surface at a high enough temperature?

³ Cf. Langmuir and Villars, *J. Amer. Chem. Soc.*, 1932, **53**, 486; Roberts, *Proc. Roy. Soc., A*, 1935, **152**, 460.

The tungsten filament was first cleaned by heating to 1800°C . for 40 min. At a filament temperature of 635°C ., the half-life of phosphorus was 6.0 min. 0.0178 mm. of oxygen were added and the tap connecting the reaction vessel and the phosphorus reservoir kept open in order to maintain the pressure of phosphorus vapour at a constant value during the run. After 20 min. 0.012 mm. O_2 had been used up. The half-life of oxygen was therefore 15 min., since the rate of oxidation is first order with respect to the oxygen pressure,³ which is more than twice that of the phosphorus at the same filament temperature. The reaction vessel was pumped out and a run with phosphorus yielded a half-life of 5.9 min. 0.0234 mm. O_2 were then admitted alone to the reaction tube. The pressure fell to 0.0299 mm. after keeping the filament at 635°C . for 21 min. The oxygen was pumped out and it was found that the half-life of the phosphorus had increased to 11.2 min. After heating the filament to 1800° for 36 min. in vacuo the half-life returned to 4.8 min. The filament was once more poisoned. The temperature was then raised and at 890° the half-life of the phosphorus was 1.8 min., the calculated value for a clean filament being 0.06 min. On reducing the temperature to 635° , the half-life could not be measured. Finally, heating the filament to 1800° restored its former activity the half-life of phosphorus returning to the value 6.1 min. at 635° .

The conclusions to be drawn from these experiments are the following. Oxygen may poison the filament at temperatures normally used for cleaning up phosphorus, but when phosphorus vapour is present and the chain reaction between P_4 and O_2 proceeds, the filament is in some way not subject to attack. The possibility of starting chains by reactions (b) and (c) is therefore ruled out. In order to explain the fact that phosphorus prevents oxidation of the filament, it would be necessary to assume that at these temperatures, phosphorus is more strongly adsorbed on tungsten than is oxygen. Again, since the rate at which oxygen disappears is less than that at which P_4 molecules are dissociated, the chains cannot be started by P_4 molecules, for, in this circumstance, the rate at which oxygen would be consumed would be equal to the rate of dissociation multiplied by the chain length which is about 5 under the experimental conditions employed above.⁴ That is, the half-life of oxygen would have been 1.2 min. compared with 15 min. observed. These experiments rule out scheme (a) on p. 1020. It seems, therefore, that (d) is the only possible mechanism, namely that the orientation of the phosphorus-oxygen layers each of which must be saturated to conform with the zero order of the reaction, is diagrammatically $\text{W}-\text{P}-\text{O}$.

The Interaction of Phosphorus Vapour with an Oxygen-Covered Filament.

With the clean filament the half-life of phosphorus vapour was 5.9 min. On heating to 850° in oxygen at 0.0404 mm. for 10 min. the oxygen pressure fell to 0.0174 mm. Table I. shows the sequence of runs carried out with the filament in this condition.

First the temperature had to be raised to 1300°K . before appreciable clean up could be measured. At 1030° it was faster, but on returning to 1273° the half-life had fallen from 5.8 to 0.9 min., showing that part of the oxygen film is removed, but not sufficiently to allow of the half-life being measured at 908° . As may be seen from experiments 5-11, when the temperature is maintained at 1163° the half-life decreases at each run showing that the oxygen film is being progressively removed. Even eight runs at 1163° are not sufficient to remove the oxygen, since in experiment 11 the half-life is greater than 60 min. Sufficient oxygen had been removed to permit of the half-life being measured at 993° and a series of experiments (12-19) carried out in the neighbourhood of this temperature showed

⁴ Cf. Semenoff, *Kinetics*, p. 179 *et seq*.

TABLE I.—FILAMENT COVERED INITIALLY WITH ATOMIC OXYGEN. AREA OF FILAMENT, 0.282 CM.² VOL. OF SYSTEM, 157 C.C.

No.	Temp. ° K.	Half-Life Min. $t_{1/2} = 0.02$ mm.	Half-Life for Clean Filament.	Fraction of Surface Clean.
1	1273	5.8	0.038	0.0066
2	1303	0.9	0.031	0.035
3	1273	0.9	0.038	0.042
4	908	> 60	6.0	—
5	1103	8.7	0.081	0.01
6	1103	5.8	0.081	0.014
7	1103	4.3	0.081	0.019
8	1103	2.3	0.081	0.035
9	1103	1.6	0.081	0.051
10	1103	1.0	0.081	0.081
11	908	> 60.0	6.0	—
12	993	17.5	0.79	0.045
13	993	15.2	0.79	0.052
14	993	14.0	0.79	0.057
15	1033	6.8	0.35	0.051
16	1073	2.5	0.21	0.084
17	993	11.6	0.79	0.068
18	1013	7.1	0.52	0.073

that several clean up experiments could be made without affecting the oxygen layer very much. A further series of experiments is shown in Fig. 1, where $\log_{10} \epsilon$ is graphed against $1/T$; $\log_{10} \epsilon$ is the efficiency of collisions of P_4 with the surface resulting in dissociation.

It will be observed that there is not much systematic deviation of the points from the line, and hence oxygen is not removed from the surface of the tungsten. The numbers refer to the order in which the runs were made. The slope of the line corresponding to an apparent energy of activation of 27 k. cal. On the same diagram the $\log_{10} \epsilon - 1/T$ curve is shown for a clean filament, the slope of the curve in the temperature region employed in the above experiments corresponding to an apparent energy of activation of 30.0 k. cal.

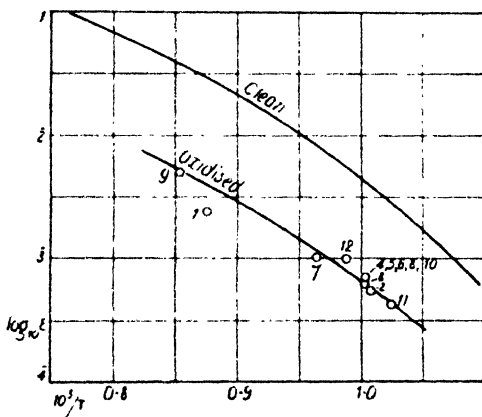


FIG. 1.

It therefore appears likely that any clean up by a partially covered oxygen surface is due mainly to the dissociation of P_4 molecules on bare portions of the tungsten. Assuming this to be the case, a calculation may be made of the fraction of the surface which is clean, in the following way. From the upper curve of Fig. 1 the half-life for the clean up at any temperature may be calculated if it is measured at only one temperature. The values (t_1'') for the present system are shown in column 4 of Table I. The ratio of the value on a clean surface (t_1'') to that on a partially oxidised surface (t_1') is shown in column 5. This, then, is the fraction of the surface free from oxygen. It will be seen that the extent of the clean surface gradually increases at temperatures above 1100°, whereas at 950° the fraction of the surface clean remains substantially

constant. An approximate estimate may also be made of the collision efficiency for the removal of oxygen atoms by P_4 molecules. In experiments $5.11 t_{\frac{1}{2}}''/t_{\frac{1}{2}}'$ increased from 0.009 to 0.081, which corresponds to the removal of 9.2×10^{12} atoms of oxygen, since there are 4×10^{14} atoms per cm^2 in a complete film. During this time, about 0.1 mm. of P_4 vapour was cleaned up. The total number of collisions of P_4 with the oxygen covered surface is, assuming a mean pressure of 0.015 mm., and a total time of 24 min., 1.1×10^{21} , yielding a collision efficiency of 8.4×10^{-9} , compared with 4×10^{-2} for the dissociation of P_4 . At 1300° the number of O atoms removed by 4.7×10^{19} colliding molecules of P_4 is 3.9×10^{12} , the collision efficiency being therefore 8.3×10^{-8} . The temperature coefficient for the removal of O atoms thus corresponds to an energy of activation of 46 k. cal., which is considerably greater than that for the clean up on a bare surface.

If these assumptions are true, then the P_4 clean up may be used to measure the fraction of a tungsten surface which is bare when the greater part of it is covered with oxygen. Such a method is complementary to that in which caesium is employed to detect the presence of small amounts of oxygen on a relatively bare surface.⁵

Further Experiments on the Hetero-homogeneous $P_4 - O_2$ Reaction.

The next experiments were made to find what effect the unifilm of oxygen atoms had on the initiation of chains in $P_4 - O_2$ mixtures. With the clean filament the half-life of the P_4 at 635°C. was 6.7 min. The hetero-homogeneous reaction was followed in a manner slightly different from that used previously. Oxygen was admitted first, followed by the phosphorus and the pressures measured on the Pirani gauge. At the end of the run the P_4 was condensed out, the p_{O_2} measured, O_2 pumped out, P_4 evaporated and its pressure determined. The data are given in Table II., two clean up runs being made in between the oxidation experiments to make sure no oxidation of the filament had occurred.

TABLE II.

TIME OF EXPERIMENT, 32 MIN.

O_2 initial	0.0147	P_4 initial	0.0140
O_2 final	0.0049	P_4 final	0.0026
$t_{\frac{1}{2}}(O_2)$	9 min.	$t_{\frac{1}{2}}(P_4)$	13.2
$O_2 : P_4$ (used)		0.95 : 1	
$t_{\frac{1}{2}}$ for clean up at $635^\circ \text{C.} \approx 5.7$ min.			

TIME OF EXPERIMENT, 33 MIN.

O_2 initial	0.0181	P_4 initial	0.0087
O_2 final	0.0040	P_4 final	0.0024
$t_{\frac{1}{2}}(O_2)$	14.2	$t_{\frac{1}{2}}(P_4)$	17.8
$O_2 : P_4$ (used)		2.24 : 1	

The first point to note is that no appreciable poisoning of the filament occurs during an oxidation run, second, the half-life of the oxygen is much greater than that of the clean up, and finally the $O_2 : P_4$ ratio of the reacting gases is lower than that corresponding to the formation P_4O_{10} , or even of P_4O_6 . The lower the phosphorus pressure, however, the higher is this ratio. In addition to the oxidation, there is considerable deposition of red phosphorus which means that besides supplying molecules to initiate the chains, the tungsten can still catalyse the dissociation of P_4 molecules.

⁵ Langmuir and Villars, *J. Amer. Chem. Soc.*, 1931, **53**, 495.

If it be assumed that the trioxide is formed in the first experiment,* then the $O_2:P_4$ ratio should be 3:1, which would imply that about 60 per cent. of the P_4 molecules which are used up are deposited as red phosphorus. From these results a maximum value for the collision efficiency of the reaction $P_4 + O_2$ may be computed. The probability of a P_4 molecule reaching the walls is $e^{-L/\lambda}$, where λ is the mean free path and L is the distance the molecules diffuse in the mixture, namely 1 cm. The mean pressure during the experiment is 0.02 mm., and if the mean free path is taken to be 3 mm. $e^{-L/\lambda} = 0.037$, i.e., only 3.7 per cent. of the P_4 molecules reach the walls without making a collision with O_2 . Taking the diffusion coefficient of the mixture to be 5.7×10^5 cm²/sec., and the mean velocity of the molecules 4×10^4 cm./sec., then the number of collision on diffusing to the walls is about 20, which therefore limits the collision efficiency to a maximum value of 0.05. The higher the pressure of the oxygen the smaller is the probability of red phosphorus being deposited on the walls, as is seen by the fact that the $O_2:P_4$ ratio increases to 2.24.

On poisoning the filament once more by heating to 830° C. for 3 min. in presence of 0.05 mm. O_2 , the half-life could not be measured, nor could any oxidation ($< 10^{-4}$ mm.) be detected in 11 min. at 635° C. Heating the filament in vacuo to 1800° C. restored its former activity, the half-life of phosphorus being 5.9 min. Hence, not only does a film of atomic oxygen inhibit the dissociation of P_4 molecules, but also the formation of molecules requisite for initiating chains. At high enough temperatures—836° C.—even an oxygen covered filament cleans up both P_4 and O_2 , but the fraction of the reaction which goes by way of chains was not measured.

Summary.

The effect of oxygen on the clean up of phosphorus vapour by hot tungsten filaments has been investigated with the following results.

Covering a filament with a layer of O atoms completely inhibits the dissociation of P_4 molecules upon it. At high enough temperatures an oxygen covered filament catalyses the dissociation, the oxygen film being simultaneously removed. At lower temperatures the oxygen film is no longer removed, a fact which permits a determination of the apparent energy of activation for clean up. This agrees with that for a clean filament, and hence it is concluded that the dissociation on a partially oxidised filament occurs wholly on the clean tungsten surface.

Further investigation has also been made of the hetero-homogeneous reaction between P_4 and O_2 in presence of tungsten. Measurement of the half-life for the $P_4 - O_2$ reaction and for the P_4 clean up, show the former to be much slower thus excluding the hypothesis that chains are started by the P_2 molecules from the dissociation of P_4 . Covering the tungsten with a unilam of O atoms also inhibits the oxidation. At the temperatures used in these experiments, about 700° C., oxygen alone rapidly covers the surface with oxygen atoms. In presence of phosphorus, however, this poisoning is practically prevented. It is therefore concluded that in the $P_4 - O_2$ reaction the tungsten surface is covered with a layer of phosphorus, on top of which are oxygen atoms or molecules. The evaporation of a lower oxide from this composite layer initiates the stable chain reaction.

One of the authors (H. W. M.) is indebted to the Royal Commissioners for the Exhibition of 1851 for a Senior Studentship during the tenure of which these experiments were carried out.

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* Actually there is evidence that involatile P_4O_{10} is deposited, cf. in this connection Semenoff, *Kinetics*, p. 165.

THE VAPOUR PRESSURE OF RED PHOSPHORUS.

BY H. W. MELVILLE AND S. C. GRAY.

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The vapour pressure of a substance may be determined by two general methods, (a) direct manometric measurement of the pressure when the material is enclosed in a box, a variation of this method of especial importance at low pressures is to measure the rate of effusion of the vapour from a small hole in the box; (b) determination of the rate of evaporation *in vacuo* and subsequent calculation of the vapour pressure by means of the effusion equation, assuming that the condensation coefficient of the molecules or atoms is unity. Where comparison can be made these methods give results in agreement, provided that complications due to association or dissociation of the vapour are absent. When there are abnormalities of this nature a comparison of the two methods may then give some clue as to the mechanism of condensation and evaporation occurring at the interface.

The vapour pressures of (red) phosphorus, arsenic and to a smaller extent antimony are abnormal in the sense that the value of Trouton's constant calculated from the vapour pressure is unusually high, e.g., 37.4 for red phosphorus. Alternatively the vapour pressures are high compared with those calculated from the latent heat of vaporisation and using Trouton's constant to compute the integration constant of the vapour pressure equation. The vapour pressure of white phosphorus however is normal. From density measurements the vapour above white and above red phosphorus consists of P_4 molecules, which would imply that P_4 molecules condense on and evaporate from the surface of red phosphorus. In another paper¹ it has been shown that if P_2 molecules impinge on a red phosphorus surface they condense to form red phosphorus, no combination to P_4 occurring. It was also suggested that P_2 molecules evaporate from red phosphorus. The explanation of the abnormally high vapour pressure is then simply that in a closed system P_2 molecules evaporate from red phosphorus but as they accumulate the $P_4 \rightleftharpoons 2P_2$ equilibrium is established and since this lies almost wholly on the P_4 side, the observed pressure is mostly due to P_4 molecules.

The object of the present paper is to show that only P_2 molecules evaporate from the surface of red phosphorus *in vacuo* and that computation of the vapour pressure employing the molecular distillation technique gives values much lower than those obtained by the static method, this in turn yielding a more normal value for the Trouton constant. As will be seen below these expectations are realised and hence the conclusion is that only P_2 molecules are concerned in the evaporation and in the growth of red phosphorus.

Experimental.

The apparatus used consists essentially of two parts: one (I.) in which the phosphorus deposit is prepared and the other (II.) in which evaporation is carried out. The arrangement for deposition is shown in Fig. 1 and in

¹ Melville and Gray, *Trans. Faraday Soc.*, 1936, **32**, 271.

detail in Fig. 1*a*. A tungsten filament *F* is placed opposite the plate holder *P*. The glass plate upon which the red phosphorus is deposited is carried in this nickel wire holder. In order to define precisely the area of deposit a mica screen with a rectangular opening is fixed on the side of the plate facing the filament. Preliminary experiments showed that if the red phosphorus were deposited on a smooth glass surface then on heating in the apparatus in Fig. 2 the film invariably peeled off. This difficulty was overcome by lightly grinding the plate when the phosphorus formed a strongly adherent layer. Apparatus II. is essentially a pyrex bulb of 750 c.c. fitted with a re-entrant tube with a flat bottom on to which the phosphorus was received. This was partially filled with liquid air. About 1 cm. from the surface of the liquid air trap, the furnace for carrying the glass plate was supported by two 1 mm. nickel wires which also served to carry the current for heating the furnace. A support *S* kept the furnace assembly in position. The current leads finally passed out at a pinch seal which also carried the leads for the small platinum-platinum-rhodium thermocouple. The details of the construction of the furnace are shown diagrammatically in Fig. 2*a*. A flat iron plate 25 × 15 × 2.5 mm. served as a base on which the glass plate rested.

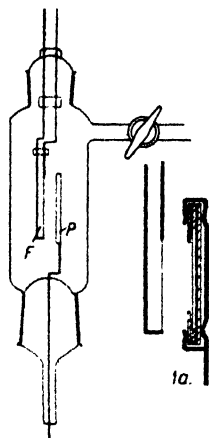
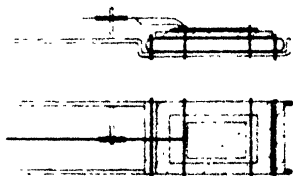
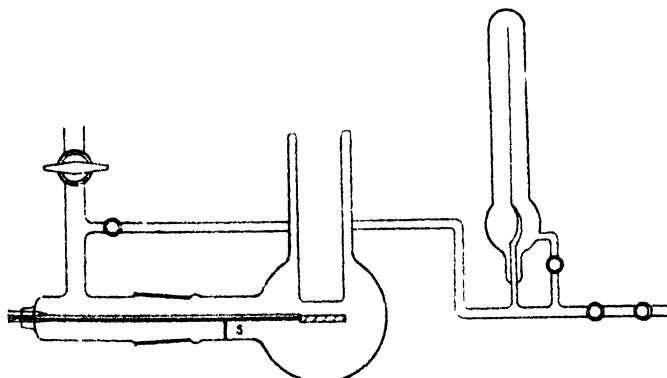


FIG. 1.

FIG. 2*a*.

The wires were 0.05 mm. thick and the junction itself was enclosed in a minute glass bead just sufficient to coat the wires. It was held in position by a molybdenum spring. Many attempts were made to fuse the glass bead

FIG. 2*b*.

containing the junction on to the glass plate, in order to obtain good thermal contact, but this was always attended by cracking of the plate once the temperature of the furnace was raised to about 400° C. The e.m.f. of the

couple was measured by a millivoltmeter. The construction of the furnace in this way gave a fairly even distribution of temperature over the surface of the plate according to visual observation when it was run red hot. It will be seen from the diagrams that the red phosphorus deposit only occupies the central portion of the plate. However, an exploration of the surface temperature was made by placing the thermocouple at various positions in the area occupied by the red phosphorus with a fixed current in the furnace windings. Even at the edge of the glass plate, the temperature was not more than 5° lower than that at the middle. Evaporation (runs) carried out with the couple in different positions gave the same values for the vapour pressure. In one or two of the distillations there was evidence that some white phosphorus was produced and it therefore became necessary to estimate its weight. For this purpose a glass spring gauge and an oxygen reservoir was attached to the evaporation bulb in order that a small quantity of oxygen could be admitted and the absorption by the oxidation of the white phosphorus noted.

This was the final form of the apparatus. The following arrangements were tried but were discarded. A movable filament system was introduced into the evaporation bulb in order to deposit the red phosphorus on the plate without having to remove the glass plate. This was unsatisfactory because the red phosphorus was sometimes deposited on the sides of the bulb and on the liquid air trap itself. The plate was also heated by radiation using a furnace consisting of several spirals of tungsten backed by a nickel reflector. Temperature control was difficult, the wire having to be run at 2000°C . and the whole bulb got unduly hot. Attempts to use a bifilar suspension for observing the change in weight of the plate were also abandoned.

Results.

The procedure for carrying out a run was as follows: A clean ground plate (weight $0.1\text{--}0.2\text{ gm.}$) weighed on a micro-balance to 10^{-5} gm. was fixed in the holder shown in Fig. 1a and inserted in the deposition apparatus. After pumping out for several hours, phosphorus vapour was admitted to a pressure of 0.02 mm. and the deposition commenced by heating the filament. Deposition of 1 mgm. on 1 cm.^2 required about 12 hours, the pressure of phosphorus being maintained at 0.02 mm. The plate was then removed and weighed. To make sure that no appreciable volatilisation of the phosphorus occurred and also that no oxidation had taken place during its transference from apparatus I. to II., the plate was reweighed 24 hours afterwards. Invariably the weight was within 10^{-5} gm. of that previously recorded. Had there been evaporative, there would have been a decrease in weight; oxidation would have led to an increase.

The furnace having been previously outgassed, the plate was placed in position and after evacuation of the bulb, liquid air was run into the tube. During evaporation, which occupied 1 to 3 hours, the pressure in the bulb did not rise above 10^{-4} mm. The mean free path of the P_2 molecule is about 50 cm. at this pressure and since the molecule has only to traverse a distance of 1 cm. , the chance of its colliding with other molecules on the way is small. Reweighing the plate completed the experiment.

Experiments were also made with blank plates to make sure that the plate itself did not decrease appreciably in weight. The weight of the plate was about 0.2 gm. At the highest temperatures a decrease of $1 - 2 \times 10^{-5}\text{ gm.}$ was the largest recorded.

Another check, though less accurate, was made in the following way. A small circular deposit, 3 mm. in diameter was formed on the plate and the evaporation carried out in the usual manner. On account of the cosine law of evaporation, the deposit on the liquid air-cooled surface thins out towards the edges with the result that a set of Newton's rings develops on the liquid air-cooled surface. Four rings could be observed and from their diameter an approximate estimate could be made of the weight of

the red phosphorus collected, assuming the refractive index to be 1.5. This agreed within 25 per cent. of that determined by direct weighing. Furthermore this allowed of a continuous observation of the rate of evaporation.

Typical results are shown in Table I. Experiments 4 and 7 were second evaporations from the same plate. The vapour pressures in the sixth column of the Table were calculated from the Herz-Knudsen equation

$$p = 17.4 \sqrt{\frac{T}{M}} \cdot m$$

where p is the pressure in millimetres of mercury, M is the molecular weight of the vapour and m the mass in grams evaporating per sec. per cm^2 of surface. The following two assumptions were made (a) that the condensation coefficient of P_4 molecules on red phosphorus is unity, and (b) that the effective surface is equal to the projected geometrical surface. The vapour pressure of red phosphorus determined by the static method is computed from the formula

$$\log_{10} p(\text{mm.}) = -\frac{5610}{T} + 11.061.$$

It will be observed that the new values are considerably lower than the older data, which is in accordance with the introductory statements. In Fig. 3, $\log_{10} p$ (mm.) is plotted against $1/T$, this giving a straight line with a slope corresponding to an energy of evaporation of 20 kg. cal.—not much lower than 25.6 kg. cal. from the temperature coefficient of the pressure of P_4 molecules above red phosphorus. The extrapolation required to calculate Trouton's constant from the new data is so large that no quantitative use could be made of the calculation. In a qualitative way however it is obvious that the smaller vapour pressures would give a smaller value for Trouton's constant than that (37.4) derived from the data quoted in the last column of Table I.

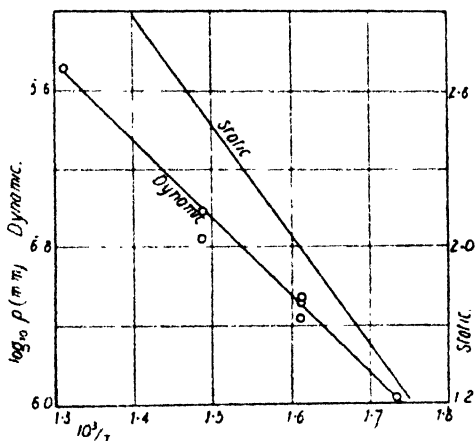


FIG. 3.

TABLE I.

No. of Experiment.	Temperature of Evaporation, °C.	Area of Evaporation, cm^2 .	Weight Evaporation, gm.	Time of Evaporation, min.	Vapour Pressure, mm.	Vapour Pressure Static Method, mm.
1	480	1.12	0.00049	8	5.5×10^{-6}	3490
2	410	1.12	0.00046	60	6.6×10^{-6}	630
3	400	1.20	0.00048	60	6.4×10^{-6}	480
4	400	1.20	0.00066	60	8.8×10^{-6}	480
5	350	1.20	0.00022	62	2.7×10^{-6}	102
6	350	1.20	0.00028	62	3.5×10^{-6}	102
7	350	1.20	0.00010	21	3.6×10^{-6}	102
8	305	1.12	0.00016	124	1.0×10^{-6}	21.5

After some of the evaporations, oxygen was admitted to the evaporation bulb, the tap to the pump having been closed and the liquid air allowed to evaporate. Sometimes a momentary flash due to the oxidation of white phosphorus was obtained, but the amount of oxygen consumed indicated that less than 5 per cent. of the total phosphorus evaporated consists of P_4 molecules. The presence of white phosphorus was most pronounced when the evaporation was carried out with a clean liquid air-cooled surface. After the latter had become covered with red phosphorus practically no white modification could be detected. It would seem therefore that only a fraction of the P_4 molecules tend to combine on striking a glass surface. This is in agreement with previous observation on the clean-up of phosphorus vapour. Reproducible and constant results were only obtained when the surface of the reaction vessel had become covered with a uniform film of red phosphorus.

Summary.

A redetermination of the vapour pressure of red phosphorus has been made by evaporation in a vacuum. Application of the Herz-Knudsen effusion equation to the results gives values for the vapour pressure about 10^7 times lower than the normal static method. The new values are given by the equation

$$\log_{10} p \text{ (mm.)} = -\frac{4110}{T} + 1.1.$$

The reason for the discrepancy is due to the fact that although P_4 molecules condense on and evaporate from red phosphorus, the equilibrium $P_4 \rightleftharpoons 2P_2$ is set up in a closed system. At temperatures normally employed the equilibrium is almost wholly on the P_4 side and hence in the static method the pressure is due almost wholly to P_4 molecules. In the molecular distillation method no opportunity is given to the molecules to combine to P_4 and therefore the apparent vapour pressure is much smaller.

Erratum.

In the first paper of this series¹ the heat of transformation of white to red phosphorus was erroneously taken as 4 kg. cal. per gram molecule (P_4) whereas in fact this value refers to the gram atom. This alters slightly the calculation of the heat of desorption of $P_2(\lambda_p)$ from red phosphorus, see page 274 *loc. cit.*¹ Taking the heat of dissociation of P_4 to $2P_2$ to be 30 kg. cal. then

$\lambda_{p_2} = 29.8$ kg. cal. from the thermo chemical cycle

and 27.9 kg. cal. from the apparent heat of evaporation of red phosphorus.

The corresponding values if $P_4 \rightarrow 2P_2$ is 50 kg. cal. are 39.8 and 37.8 kg. cal. respectively. The agreement between the two methods of calculation is even better than that formerly obtained.

The authors are indebted to Professor E. K. Rideal and Dr. E. B. Ludlam for critical discussions during the progress of this work. One of them (H. W. M.) thanks the Royal Commissioners for the Exhibition of 1851 for a Senior Studentship. The experiments were made in the Chemistry Department of the University of Edinburgh.

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KINETICS OF SIMULTANEOUS POLYMERISATION AND RING FORMATION.

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In a recent article¹ on this subject, it was stated that the velocity constant k_1 , measured between the limits of 10 and 70 per cent. conversion, corresponds to the purely monomolecular ring closure reaction, even though 25-35 per cent. of polymers are formed at the reaction. This conclusion is based on a second statement, unsupported by any experimental data, according to which "the essential part of the secondary polymers is formed between the limits of 60 and 100 per cent. conversion."

In contrast to this, we have shown, as a result of numerous experimental researches described and discussed in detail elsewhere,² that the determination of the velocity constant in a monomolecular ring-closure reaction (on the basis of changes in the functional groups and in those cases where it leads to rings of more than six members) is unequivocal *only if no polymers* can be traced, even if the reaction seems to be a first order reaction with a velocity independent of the initial concentration.

A reaction of the first order, or a reaction velocity independent of the initial concentration is, therefore, no proof at all that the reaction has proceeded as in infinite dilution. On the contrary, it seems to be typical of ring-closure reactions that, between the limits of 10 and 70 per cent. conversion, they are always of the first order, even if they depend on a previous bimolecular reaction.³

The velocity of polymerisation cannot, moreover, be estimated from a graphic representation of the reaction velocity; for, if the polymerisation is a primary one, it can only take place at the beginning of the reaction, up to about 10 per cent. conversion.⁴ At this stage, however, the chances of error are highest and graphical appreciation is therefore inaccurate. If, in addition, a secondary polymerisation should occur, even this approximate appreciation becomes impossible. On the one hand, the primary polymerisation, as several experiments have shown, tends to reduce the reaction velocity after 10 per cent. conversion^{4, 5} and, on the other hand, the secondary polymerisation (which, as we seek to prove below, reaches its highest velocity at about 50 per cent. conversion) increases the velocity between 30 and 70 per cent. conversion. In these circumstances, any attempt at determining the velocity constant graphically, must be considered illusory.

¹ G. Salomon, *Trans. Faraday Soc.*, 1936, **32**, 169.

² M. Stoll, A. Rouvé and Stoll-Comte, *Helv.*, 1934, **17**, 1289; 1935, **18**, 1087.

³ M. Stoll and A. Rouvé, *Helv.*, 1936, **19**, 253.

⁴ *Ibid.*, 1935, **18**, 1097.

⁵ *Loc. cit.*,³ page 1297, Table III.

Consider the case ⁶ where the ring closure product B reacts with the starting material A, and forms a secondary polymer AB. The velocity of this secondary polymer reaction, $\frac{dC_{AB}}{dt}$, will depend on the concentration of the starting material C_A and on the concentration of the ring closure product C_B , $\frac{dC_{AB}}{dt} = k_3 \times C_A \times C_B$. The velocity will be highest when the product of the two concentrations reaches a maximum. Since $C_A + C_B = 100 - C_{AB}$, this will be the case when

$$50 \geq C_A \geq \frac{100 - C_{AB}}{2} \geq C_B.$$

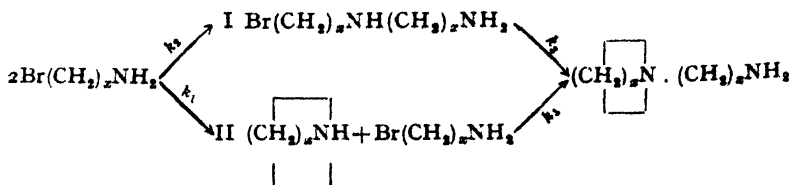
If the maximum should occur at 60 per cent. conversion, then the concentration of the secondary polymers must have reached 20 per cent. of the starting material. *Moreover, if the reaction yields (at complete conversion) 25.35 per cent. polymers, then they have been mainly produced before 60 per cent. conversion (conversion = $100 - C_A$).*

TABLE I.

C_A	C_B	C_{AB}	Difference.	$C_A \times C_B$	$100 - C_A$
100	0	0	—	0	0
87	10	3	3	870	13
72	20	8	5	1440	28
56	30	14	6	1680	44
50	34	16	2	1700	50
40	40	20	4	1600	60
25	50	25	5	1250	75
11	60	29	4	660	89
0	68	32	3	0	100

From this and from Table I. (which is merely schematic), it follows that the highest velocity of formation is found, not between the limits of

⁶ In order to explain the formation of appreciable quantities of polymers AB during the cyclisation reaction of bromamines, G. Salomon ¹ considers only one of the two possible reactions



We are of the opinion, that it is impossible by means of kinetic analysis to exclude entirely one or the other of the two reactions. It is most probable, that the two reactions proceed simultaneously, a fact which cannot be without its influence on the monomolecular velocity constant k_1 .

60 and 100 per cent., but between 25 and 75 per cent. conversion. The velocity constant k_1 measured between 10 and 70 per cent. conversion, therefore contains to a large extent also the velocity constant k_2 of the secondary polymer reaction.

Moreover, if one takes into consideration the fact that the occurrence of a primary polymer reaction, which would take place mainly in the first phases of the reaction (0-10 per cent. conversion) cannot be excluded (for the reasons mentioned above)⁶ it becomes clear that the velocity constant of a reaction in which an appreciable quantity of polymers is formed, cannot in any way be considered as representing the velocity constant of the monomolecular ring formation. There is therefore no sufficiently accurate foundation for any mathematical treatment or general consideration of the ring-closure problem (more especially the calculations of the Arrhenius constants)⁷ based on such an assumption.

Knowing that it was practically impossible to obtain pure velocity constants for ring-closure reactions, we introduced some time ago⁸ the "cyclisation constant," i.e. the quotient k_1/k_2 , as a measure of the facility of ring formation.

If c is the concentration of the starting material, and Y the quotient (monomeric ring-closure product) / (total primary polymers) at complete conversion, then the cyclisation constant k_1/k_2 is determined by the equation⁸

$$\lg\left(1 + \frac{c \cdot k_2}{k_1}\right) = \frac{Y \cdot c}{1 + Y} \cdot \frac{k_2}{k_1}$$

and can readily be obtained by a quantitative analysis of the reaction products. Again, in this case, however, the determination of the cyclisation constant, is limited to ring-closures for which the primary monomolecular reaction product is stable, and does not undergo any important transformation, as, for instance, do the cyclic imines.

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Firmenich & Co. Successors,
Geneva.*

⁷ *Loc. cit.*⁵ As the yield of the cyclisation of hexamethylenbromamine in 0.005 molar aqueous solution does not reach 100 per cent., it appears most probable that the too high activation constant Z_4 (G. Salomon, *loc. cit.*¹) is due, not to a particularly high probability of the ring position but, rather, to an "impure" monomolecular velocity constant, and this in spite of the concordance between the calculated and observed values.

⁸ M. Stoll, A. Rouvé and G. Stoll-Comte, *loc. cit.*⁵ p. 1292; *loc. cit.*⁴ p. 1099.

THE EXCHANGE OF DEUTERIUM BETWEEN DEUTERIUM HYDROXIDE AND ETHYL ALCOHOL.

BY W. J. C. ORR.

Received 11th May, 1936.

It has generally been supposed that the exchange reactions of deuterium between water and the alcohols are very rapid. Some preliminary calculations indicated that the rate might, in neutral solutions, be open to observation, and at the outset several attempts were made to follow

the progress of the reaction: $C_2H_5OH + HOD \rightleftharpoons C_2H_5OD + HOH$ by means of such physical properties as refractive index, viscosity, and electrical conductivity in the presence of dilute acid. No significant changes were observed, from which it was concluded that either the change in property observed was very small, or the reaction very rapid. Attention was then turned to the determination of the equilibrium constant of the reaction and a method was developed in which a sample of the water from the equilibrium mixture was removed for analysis as $CaSO_4$ hydrate. It was found in these experiments that the extent of the exchange varied with the time of contact prior to the addition of the $CaSO_4$, and it appeared that about 18 hours was required for the establishment of equilibrium at $25^\circ C$.

Experimental.

Procedure.—Solutions of ethyl alcohol and 20 per cent. deuterium hydroxide were made up by weight in stoppered tubes and placed in a thermostat at $25^\circ \pm .01^\circ C$. To determine the concentration of deuterium in the water in a given mixture at a given time 3.4 grms. anhydrous $CaSO_4$ was added which removed a fraction of HOD as hydrate. The hydrate was rapidly filtered on a sintered glass crucible, dry air being drawn through the precipitate for 45 minutes under a pressure reduction of about 40 mm. The $CaSO_4 \cdot x$ HOD was then dehydrated at 150° for $1\frac{1}{2}$ hours, and the liquid analysed. That no appreciable fractionation of HOD occurred in the above process¹ is shown in the following typical experiment. 4.40 grms. $CaSO_4$ were added to 4.0 c.c. 20.4 per cent. HOD. 3.47 grms. of the hydrated salt were collected from which 1.05 c.c. HOD, of D-concentration 20.2 per cent., were obtained.

The formation of the hydrate is not instantaneous but takes place during 30 minutes so that the sample of water removed represents the average concentration of D in the water portion of the reacting mixture during this time.

The ethyl alcohol was dried for fourteen days over CaO , then two days over Ca and slowly distilled, a middle fraction boiling at $77.2^\circ C$. (760 mm.) being collected under anhydrous conditions for these experiments.

20 per cent. DOH, obtained by dilution of the I.C.I. 99.95 per cent. product was twice distilled and outgassed. The D-content of several samples was determined for calibration purposes (to within .01 per cent.) by density measurements using a 14.0 c.c. pycnometer.

A.R. $CaSO_4$ was freshly dehydrated under reduced pressure at $180^\circ C$.

Analysis.—The yield of water to be analysed varied between 0.5–1.0 c.c. and usually contained traces of alcohol (< 0.4 wgt. per cent.). In order to analyse the mixture for D in the presence of alcohol, density and interferometer measurements were made in co-operation. With a pycnometer of 0.45 c.c. capacity the D-content was given by the calibration equation (mol. per cent. D) = $0.209 W (\pm 0.2)$, where W is the difference, in 0.1 m. grm. units, of the weight of the pycnometer filled with a given sample of heavy water and when filled with ordinary water. The calibration equation for measurements with a 1 cm. cell of a Rayleigh Interferometer was (mol. per cent. D) = $-0.0629 I (\pm 0.1)$ where I is the number of drum divisions shift when a heavy water sample is compared with ordinary water.

Calibration solutions of known quantities of alcohol in H_2O and in 18.6 per cent. HOD were made up, and the difference in density and interferometer reading compared with H_2O in the first case and 18.6 per cent. HOD in the second, were measured. These differences, plotted in Fig. 1, show that the addition of alcohol in a given proportion to H_2O and HOD (up to 18.6 per cent.) produces the same change both in density and inter-

¹ Cf. Day, Hughes, Ingold and Wilson, *J. Chem. Soc.*, 1934, 1593.

ferometer reading. Thus, since the addition of alcohol to water increases the refractive index and decreases the density, while the addition of HOD decreases the refractive index and increases the density, a unique value for the D-content can be found. If a sample of water containing EtOH gives

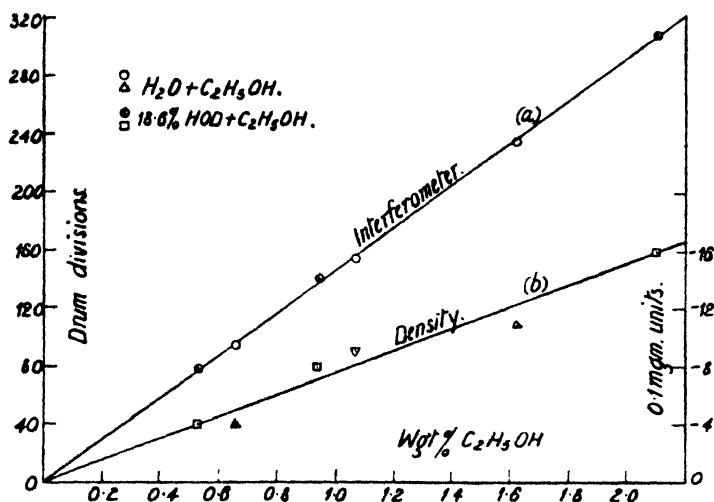


FIG. 1.

an interferometer reading I , and a density difference W , compared with ordinary water, then

$$(\text{mol. per cent. D}) = -0.0629 (I - x) = 0.209 (W - y)$$

where $x/y = a/b = -19.2$, a and b being the slopes of the curves so labelled in Fig. 1.

Results.

Initial Per Cent. HOD.	Wgt. EtOH grms.	Wgt. HOD grms.	Vol. of Soln. c.c.	Time of Re- action Hours.	I Drum Divisions.	W o'1 mgrms.	Equil. Per Cent. HOD.	Grm. mol./litre.				α
								a.	b.	c.	x.	
21.74	3.3667	5.5172	9.44	2	-107.5	44	19.4	7.74	6.98	25.13	0.74	0.44
20.9	2.0664	3.9926	6.38	3.8	-84	40	18.0	7.04	7.18	27.17	0.97	0.72
20.9	3.7732	8.8250	13.16	6.8	-122	42	18.0	6.23	7.70	29.15	1.06	0.93
20.9	3.7570	6.4450	10.81	26	-133.5	40	16.75	7.53	6.84	25.91	1.36	1.10
20.9	3.7170	6.0101	10.34	33	-124.1	39	16.4	7.81	6.67	25.26	1.41	1.12
20.9	2.2521	3.7694	6.39	108	-119.7	39	16.6	7.65	6.78	25.65	1.39	1.11

The exchange ratio, α , in the above Table is defined as

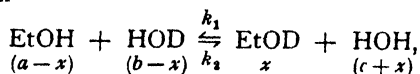
$$\alpha = \frac{x(c+x)}{(a-x)(b-x)} = \frac{[\text{EtOD}][\text{HOH}]}{[\text{EtO}][\text{HOD}]},$$

where $[\text{EtOD}]$, etc., are the molecular concentrations of each species in the mixture at time t . Since there is a probable error of ± 0.2 mol. per cent. in the determination of the equilibrium D concentration the values of α are uncertain to ± 2 per cent.

From Fig. 2, which shows the variation of α with time, the equilibrium distribution $\alpha_e = 1.11$.

Discussion.

In the reaction



the rate of formation of EtOD may be expressed analytically as follows :

$$\frac{dx}{dt} = k_1(a-x)(b-x) - k_2x(c+x) \quad (1)$$

At equilibrium $\frac{dx}{dt} = 0$,

$$\therefore \frac{k_1}{k_2} = \frac{x(c+x)}{(a-x)(b-x)} = \alpha_e (= 1.11). \quad (2)$$

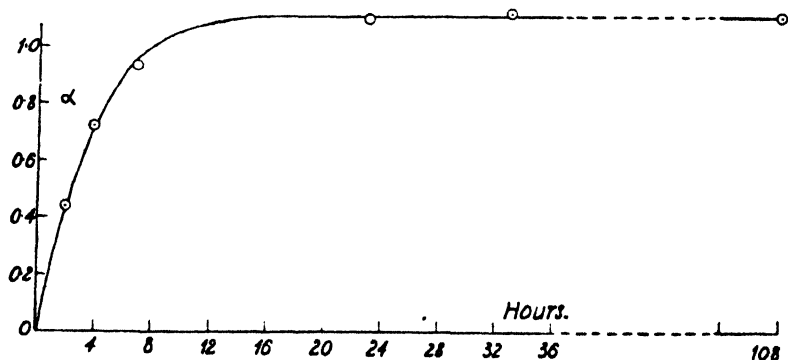


FIG. 2.

Substituting $k_2\alpha_e$ for k_1 in equation (1) and integrating gives the following result :

$$k_2 = \frac{2.303}{\beta(\alpha_e - 1)t} \log_{10} \frac{2\lambda - x(K - \beta)}{2\lambda - x(K + \beta)},$$

where

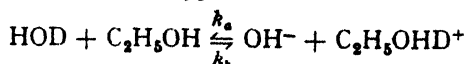
$$K = \frac{1}{\alpha_e - 1}[(a+b)\alpha_e + c]; \quad \lambda = \frac{1}{\alpha_e - 1}\alpha_e \cdot a \cdot b; \quad \beta = \sqrt{K^2 - 4\lambda}.$$

Since $\alpha = \frac{x(x+c)}{(a-x)(b-x)}$, α can be evaluated numerically as

a function of t when k_2 is given a definite value. The curve drawn in Fig. 2 is that calculated from the above equations, the value $k_2 = 2.2 \times 10^{-6}$ being chosen to give the best fit with the experimental points. Taking account of the possible error in the α -values one has

$$\text{and from (2)} \quad \begin{aligned} k_2 &= 2.2 \pm 0.2 \times 10^{-6} \text{ (litres/grm. mol. sec.)} \\ k_1 &= 2.4 \pm 0.2 \times 10^{-6} \text{ (litres/grm. mol. sec.)} \end{aligned}$$

The order of magnitude of these figures appears to be roughly in accordance with what is to be expected if the initial step in the exchange reaction is an ionisation of the type



Assuming, in the first place, that the mixture of HOD and EtOH is ionised to the same extent as water, the concentrations of OH^- and

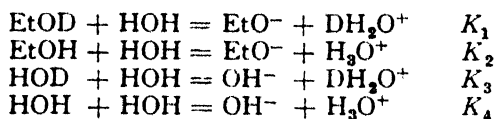
$\text{C}_2\text{H}_5\text{OHD}^+$ are 10^{-7} gram. mols./litre, and HOD and EtOH, 55.5 and 17.1 gram. mols./litre respectively, then,

$$K = \frac{k_a}{k_b} = 1.05 \times 10^{-17}.$$

The activation energy of the recombination reaction may be expected to be small: if it be assumed to be zero, then $k_b = z$, where z is the collision factor for a bimolecular reaction, an average value of which is 2.77×10^{11} (litres/gram. mol. sec.).²

Hence $k_a = 2.8 \times 10^{-6}$ (litres/gram. mol. sec.).

From the equilibrium value, α_e , the ratio of the ionisation constants of EtOH and EtOD may be calculated, the equilibria involved being as follows:



From the above equations it is evident that

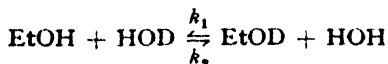
$$\frac{K_2}{K_1} \frac{K_3}{K_4} = \frac{[\text{EtOD}][\text{HOH}]}{[\text{EtOH}][\text{HOD}]} = \alpha_e = 1.11.$$

Now according to Abel, Bratu and Redlich,³ $\frac{K_3}{K_4} = 1 - 1.41x + 0.57x^2$, where x is the mol. fraction of deuterium. In the present experiments $x = 0.083$, thus $\frac{K_3}{K_4} = 0.89$ and $K_2 = 1.25 K_1$.

Summary.

1. It has been found possible to measure the rate of exchange of deuterium between ethyl alcohol and deuterium hydroxide by using CaSO_4 to remove samples of DOH from the reacting mixture.

2. The equilibrium constant, α_e , of the reaction



is found to be $= 1.11$, the rates of the forward and backward reactions being

$$k_1 = 2.4 \pm 0.2 \times 10^{-6} \text{ (litres/gram. mol. sec.)}$$

$$k_2 = 2.2 \pm 0.2 \times 10^{-6} \text{ (litres/gram. mol. sec.)}.$$

These values are of the order expected theoretically on the grounds that the exchange proceeds ionically.

3. From the equilibrium distribution ratio, α_e , the ratio of the dissociation constants of EtOH to EtOD in presence of 16 per cent. HOD is found to be 1.25.

I wish to thank Dr. J. A. V. Butler for suggesting this problem and for his advice and encouragement during the course of the work. I have also to express my gratitude to the Carnegie University Trust for a Scholarship, to the Moray Fund for a grant for the purchase of heavy water, and to Messrs. Imperial Chemical Industries for a grant by which the Interferometer was purchased.

REFERENCES.

² Moelwyn-Hughes, *Kinetics of Reactions in Solution*, p. 78.

³ *Z. physik. Ch. A*, 1935, 173, 353.

REVIEWS OF BOOKS.

Flame. By O. C. DE C. ELLIS and W. A. KIRKBY. (London, Methuen. Pp. vi + 106 + 15 figs. 3s. net.)

The Methuen Monographs on Chemical Subjects usually provide interesting fare and the present volume is not an exception. There are many aspects of the subject of flame and it is hardly possible for one individual to speak authoritatively on all of them. The authors direct their attention mainly to the behaviour of flame as an entity and to an examination of its various shapes and movements in many kinds of vessels. The phenomena occurring ahead of and behind the flame front are examined in considerable detail, and in their elucidation of these matters the authors have drawn on the wealth of experimental technique and data made available by the Safety in Mines Research Board. The authors' treatment of "afterburning" is of particular interest and contains much that is original. Ignition phenomena and the flame limits are thoroughly discussed but chemical mechanisms in the modern sense are dismissed in seven pages. There is, nevertheless, a good deal of novelty in the ideas presented, and the book is welcome if only for the clear account it gives of flame movement and associated phenomena in closed vessels. There is a valuable bibliography.

Phenomena in High Frequency Systems. By AUGUST HUND. (McGraw Hill, London, 1936; 594 pages, appendix, and index. Price, 36s.)

This book deals almost exclusively, but in great detail, with the theory of the generation, transmission, and reception of radio frequency currents. Except for the two chapters on the ionised upper atmosphere and piezo-electric phenomena, and a brief account of plasma oscillations, practically no reference is made to high frequency phenomena depending on the physical and chemical properties of substances for example, the variation of the dielectric constant and the dielectric loss with frequency.

R. W. L.

Schwimmaufbereitung. By W. PETERSEN. (Theod. Steinkopff, Dresden, 1936. Pp. xii and 300. Price, 18 RM; Bound, 19.50 RM.)

This is a very good book. The author has not hesitated to attack the difficult question of wettability and I hardly know of any equally clear exposition on interfacial tensions and their interaction, on adhesion, on the problems related to contact angles and their determination, to linear and laminar adsorption, etc. He also does not make the mistake, so frequently found in general treatises on flotation, of overrating one side of the phenomena involved and thus developing an "adsorption" or a "chemical" or an "electrical" theory of flotation; he bears in mind that all these factors, and others, come into play and does not forget that his task consists in giving a well-balanced description of these manifold effects and

their intricate connexions. Although Petersen is obviously keenly interested in the theoretical side of his subject, he by no means neglects experimental facts and thoroughly discusses a great number of collectors and frothers, many special problems in "mineral separation" and technical devices to effect flotation.

The flotation industry is in a pre-eminent position as depending on the fundamental importance of capillary chemistry and yet involving large capital expenditure. Nevertheless, physical chemists cannot boast that they were the first to introduce and devise these methods; they are almost entirely due to engineers. Surface chemistry has proved its value only in the surprising specialisation and subtlety which have been developed in recent years.

H. F.

Review of Inorganic Chemistry. By NIELS BJERRUM. (William Heinemann Ltd. Pp. vi + 317. 7s. 6d.)

Although this is intended to be an elementary text-book, it is one which can be read with pleasure and profit by any chemist, and so well has the translation been done that the reader does not feel that the book was not originally written in English.

In the reviewer's opinion, the book is not suitable for those who are just beginning the study of chemistry, but should be very useful to students who have already passed the intermediate stage. The reasoning is too close and concentrated for a beginner, and theories are stated somewhat too dogmatically and without sufficient reference to the experimental and historical foundations.

The book is admirable as a summary of modern chemical theory and of the more important facts relating to the commoner elements. The modern views of acids and bases are made clear and emphasised, as was to be expected, in a book emanating from Copenhagen. Most important theoretical matters are considered briefly and serious students of chemistry will find the book a helpful supplement to their lectures, but they must bear in mind that they will need to become acquainted with more of the hum-drum facts of chemistry than will be found in it.

H. B.

Introduction to Quantum Mechanics (with Applications to Chemistry). By LINUS PAULING and E. BRIGHT WILSON. (McGraw-Hill Publishing Co., London, 1935. Pp. xiii + 468. Price 30s.)

The Quantum Theory of Valency. By W. G. PENNEY. Methuen's Monographs on Chemical Subjects. (Methuen & Co., Ltd., London, 1935. Pp. vi + 95. Price 2s. 6d.)

The Introduction to Quantum Mechanics, which has been written by Linus Pauling and E. Bright Wilson, fulfils a long-felt need. Its aim is to provide sufficient quantum mechanics to understand the advances which are now being made in the theory of chemical bonds. It does not demand an extensive knowledge of mathematics but it does assume that the reader is anxious to understand the mathematical applications of

quantum mechanics and is willing to follow the necessary steps in the argument if suitably presented. No better guide could be recommended to those anxious to study modern developments in theoretical chemistry.

The Schrödinger equation, the interpretation of wave function and the auxiliary restrictions placed upon it, are introduced as fundamental postulates—a series of working rules, from which results can be predicted and compared with experimental data. A number of simple examples are worked out, in particular the wave functions of the hydrogen-like atom. A thorough knowledge of these is indispensable to an understanding of electronic structure of atoms and molecules, for they are used as a basis for almost all applications of quantum mechanics to molecular problems. The standard methods of passing from simple known systems to other more difficult unknown systems involve the use of the perturbation theory and the variation method. These are described in detail and a number of informative and illuminating examples are worked out.

Two subjects of great importance are then dealt with: one the method of dealing with many electron atoms and the other the structure of simple and complex molecules. The important development made by Slater in the treatment of complex atoms is described in detail, and this not only shows how the multiple structure of atoms can be found but also prepares the way for the theory of valency links. The important concept of resonance, used extensively by Pauling in chemical phenomena, is described—but only briefly. Many readers would doubtless have welcomed a further discussion of this subject and more examples. The method of molecular orbitals is only briefly referred to. None the less the book brings the reader to the stage when he can understand recent developments and for this reason is likely to find an appreciative circle of readers. The reviewer thinks so highly of it as an introductory book that he has recommended it to all his students.

The monograph by Mr. Penney carries out the difficult task of putting into descriptive language the new ideas which are at the basis of the quantum theory of valency and does it with conspicuous success. The treatment is necessarily concise owing to the limited space available in a small monograph, and those readers who approach the subject for the first time must expect to take some parts of the book for granted (particularly in the chapter on "The Method of Localised Pairs"). A close reading of the book will, however, convey a very good idea of the successes and limitations of the present theory of valency.

J. E. L.-J.

A GENERAL DISCUSSION ON DISPERSE SYSTEMS IN GASES; DUST, SMOKE AND FOG.

THE SIXTY-FOURTH GENERAL DISCUSSION OF THE FARADAY SOCIETY was held in the Department of Chemistry of the University of Leeds from the 20th to 22nd April, 1936, inclusive.

The subject was considered under two heads :—

Part I. : The General Properties and Behaviour of Disperse Systems, composed of :—

- (a) Solid and Liquid Non-Volatile Particles, *i.e.* Smoke, Dust, Oil Fogs, etc.
- (b) Aqueous and Other Volatile Particles, *i.e.* Mist, Cloud, Hygroscopic Nuclei, Town and Country Fogs.

Part II. : The Industrial Aspects of Disperse Systems in Air and Gases.

In the absence of the President, the Chair was occupied in succession by Sir Robert Robertson and Professor F. G. Donnan, Past Presidents.

By the courtesy of the Vice-Chancellor and the Refectory Committee, the Guest Night Dinner was held on Tuesday, 21st April, in the Refectory.

At the Inaugural Meeting, the Vice-Chancellor of the University, Sir James Baillie, welcomed the Society to Leeds, and Sir Robert Robertson then introduced the overseas guests, visitors and members, who were received with acclamation. The following were so welcomed : Professor J. Firket (*Liege*), Dr. E. Hiedemann (*Köln*), Professor H. Köhler (*Uppsala*), Dr. and Frau R. Meldau (*Berlin-Charlottenburg*), Dr. J. L. van der Minne (*Amsterdam*), Dr. J. J. Nolan (*Dublin*), Dr. E. Proskauer (*Leipzig*), Professor H. Remy (*Hamburg*), Dr. P. Schuftan (*München*), Dr. H. Schmeel (*Darmstadt*), and Dr. P. Siedler (*Frankfurt a.M.*).

At the conclusion of the meeting, the thanks of those present were accorded to the overseas guests, to the Vice-Chancellor and Senate of the University, to Professor Whytlaw-Gray, Mr. Cawood, and other members of the organising committee, to the Refectory Committee, and to the contributors of papers.

The Report of the meeting, including all the papers contributed, together with the discussion thereon, appears in the following pages.

DISPERSE SYSTEMS IN GASES.

(General Introductory Paper.)

BY R. WHYTLAW-GRAY.

Received 14th April, 1936.

The subject of this discussion includes a great variety of natural and artificial systems which are described by such terms as dust, smoke, fog, fume, haze, mist and cloud. All these consist of solid or liquid material dispersed to a greater or lesser extent in gaseous media. They all show a great tendency to change and none are permanent when compared with the more familiar colloidal solutions. Thus dusts settle, smokes coagulate, and clouds dissipate by evaporation.

This characteristic instability is clearly a consequence of the physical properties of the gaseous medium, the low density and low viscosity of which offers little resistance to the movement of the particles or to molecular diffusion. Hence in these systems the particles sediment under gravity or centrifugal force, diffuse by brownian motion, and evaporate or dissolve at a much greater rate than they would were the medium liquid. It must be remembered, too, that the smaller particles suspended in gases possesses an enhanced mobility on account of the discontinuities in the medium. For example, the majority of smoke particles lie between the size limits 5×10^{-6} and 5×10^{-5} cm., radius, whilst the mean free path of the molecules in air at normal pressure is of the order of 10^{-5} cms.

For the purposes of this meeting it is convenient to consider separately the behaviour of systems of non-volatile and volatile particles. To the former category belong most dusts and smokes and some industrial fogs such as tar fogs, and to the latter the majority of natural systems such as country fogs, mist, etc., in which the particles are composed of water or of dilute aqueous solutions of hygroscopic nuclei. It is obvious that there is no clear dividing line between these two classes. Thus a sulphuric acid cloud in dry air would belong to the former and in moist air to the latter, again the particles of tobacco smoke rapidly absorb moisture and those in town air contain hygroscopic as well as carbonaceous material so that they readily condense water when the conditions are favourable. But it is evident that in many respects systems of non-volatile particles are simpler and certainly easier to investigate than those in which evaporation and condensation are additional and complicating factors.

Moreover these systems of non-volatile particles have in recent years attracted the attention of scientific workers both abroad and in this country so that a short summary of their properties may serve as a focussing point for this discussion.

Smoke.

Smoke is formed whenever the vapour of a substance of high boiling-point is diluted rapidly and cooled by admixture with a large volume

of air or any other gas. This method applies to many systems. Smokes can be formed also by chemical reactions at ordinary temperatures, indeed any reaction between gases or vapours resulting in the formation of a solid or liquid phase will when carried out in presence of a large excess of an indifferent gas produce a smoke. Smokes then are formed from molecularly disperse material, by condensation, and in its early stages the process presents an analogy to the formation of a gold sol. There is however this important difference. In the sol the gold originally molecular, condenses around nuclei to form a stable two-phase system, the degree of dispersion of which is determined by the rate of formation of nuclei and by their rate of growth. In a smoke although the process of formation is apparently analogous it results in the production of an unstable system and the primary particles formed by condensation on nuclei of the supersaturated vapour coagulate rapidly so that the degree of dispersion of the system changes continually with lapse of time.

Coagulation.

This property of continuous and spontaneous coagulation is the most striking characteristic of disperse systems in gases. The smoke particles of whatever substance they are composed stick together when brownian motion brings them in contact. Probably a high percentage of the collisions are effective and although this has not been proved by direct experiment, it has been shown that adherence results from the majority of collisions between smoke particles of different kinds with various surfaces.

By determining how the number of particles in a coagulating smoke diminish with time the course of the process can be followed quantitatively. Numerous smokes have been investigated in this way by different workers but the counting of smoke particles with the slit ultra-microscope presents unexpected difficulties and led originally to erroneous results. Several methods are now available which agree among themselves and the data obtained from these show that the coagulation of very many smokes follows a simple law. If n_1 and n_2 represent the number of particles present per c.c. at times t_1 and t_2 minutes from the formation of the system, then $1/n_2 - 1/n_1 = K(t_2 - t_1)$ where K is a constant. Thus if the reciprocal of the number of particles present in a given volume of smoke are plotted against the corresponding times a straight line is obtained.

$1/n$ denotes the average space inhabited by a particle in the smoke at any instant of time. It is termed conveniently the particulate volume and n the particulate number. Although the validity of this relationship has been questioned there is so much experimental evidence to support it, that we believe it represents the course of coagulation of the majority of smokes to at least a rough approximation.

From this expression it is easy to see that the rate at which the particles disappear by coagulation depends only on the square of the number present and the constant K , i.e. $-dn/dt = Kn^2$. In any given smoke, coagulation will be very fast in the early stages when the number concentration is high and later will fall off rapidly. A comparison of the values of K obtained experimentally for different smokes in air under normal conditions of temperature and pressure shows no striking variation. Clearly the coagulation process is to some extent independent

of the nature of the particles. The coagulation constant for any one smoke does, however, vary:—

- (a) with the average size of the particle, fine smokes coagulate faster than coarse ones;
- (b) with the size distribution or range of sizes of the particles. When the size range is small the smoke approaches to the homogeneous, and systems of this type coagulate more slowly than ordinary smokes which are as a rule widely heterogeneous;
- (c) with the form and shape of the particles and the aggregates they form.

An ideal or perfect smoke would consist initially of even-sized spherical particles which on coagulation coalesce to form progressively larger spheres. The kinetics of such a system were worked out for some many years ago by Smoluchowski.

The theoretical treatment of smokes along those lines is more complicated because smoke particles lie between size limits which are comparable with the mean free path of the molecules of the gaseous medium. The simple mobility defined by Stokes' law has to be modified by terms, taking account of the discontinuous nature of the surrounding gas.

Smoluchowski's theory thus modified does, however, reproduce quite remarkably the experimental results obtained with smokes approximating to the above ideal conditions, as Patterson and Cawood have shown in their studies of stearic acid smokes.

It can be shown that the theory for a homogeneous smoke leads to an expression similar in form to that found experimentally: K , the so-called coagulation constant, being given by $K = \frac{4}{3} \frac{RT}{\eta N} \left(1 + A \frac{l}{r} \right)$, where R = gas constant, T = absolute temperature, N = Avogadro's constant, η = the viscosity of the medium, l = mean free path of the gas molecules, r the radius of the particle, and A a constant.

Thus theory leads to the expectation that the particulate volume graph would be curved, K decreasing as coagulation proceeds. Actually the curvature is so slight for particles of the size found in homogeneous stearic acid smokes of the weight concentration used that it is doubtful whether it would be detected experimentally.

This expression also predicts the influence of pressure and temperature on the rate of coagulation as well as that of the size of particle and the viscosity of the medium. Up to the present the coagulation of smokes in gaseous media other than air has not been studied. Data, too, on the coagulation rate of small particles are scanty and the effects of temperature and pressure have hardly been investigated.

On the theoretical side the applicability of Smoluchowski's theory to ideal aerosols has been much discussed recently. Experimentally a really suitable smoke is difficult to obtain. Up to the present the nearest approximation to a perfect smoke would appear to be the homogeneous and reproducible stearic acid systems mentioned above, though a smoke such as that of paraffin in which the particles are liquid would possibly offer advantages.

Considerable progress has been made in the production of smokes for experimental purposes which approximate to homogeneity. It is clear from the nature of coagulation that a monodisperse system of primary particles can only be obtained by very rapid dilution of the molecularly disperse material.

This can be accomplished by volatilization in a rapid air blast, by chemical reaction at high dilution, or by photochemical decomposition as in the elegant method discovered by Winkel and Jander in which highly diluted iron carbonyl vapour is decomposed by light of short wave length. In all these methods even at the highest dilutions in which the weight concentration of the smoke is only of the order of a few milligrams per cubic metre, the number of particles a few minutes after the smoke is formed is several millions per c.c.

Extrapolation of the particulate volume graphs for this type of smoke shows that initially the number of primary particles must be very great.

A rough calculation from the dilution of a stearic acid smoke gives 10^{12} per c.c. and recently Fuchs and Oschman by diluting with great rapidity a sulphuric acid smoke have actually formed an aerosol consisting of primary particles. They found the number per c.c. 10^{11} and the size about 10^{-6} cms.

In these experimental smokes it is clear that the ultra-microscopic particles counted are aggregates of a large number of primary units and that the coagulation process is far advanced before counting is possible. The primary particles are amicroscopic. The possibility of obtaining stable systems of these is evident and opens up an interesting line of research. Atmospheric nuclei and large ions probably belong to this class. The rapid dilution of chimney smoke in a high wind may well form these systems and they are likely to be present in ordinary smokes in the early stages.

The rapidity of coagulation in systems of high number concentration is evident when the time taken to halve the number of particles is calculated. Using for this purpose the K value for a stearic acid smoke, viz.: 0.51×10^{-9} cm.³ sec.⁻¹ we find for a system of 10^{11} particles per c.c. $t = 0.02$ sec., for 5×10^8 per c.c. 6.6 minutes and for 10^5 per c.c. 5.5 hours. To obtain a stable system of primary particles the original smoke must be diluted with 10^5 or 10^6 volumes of air in a fraction of a second.

So far practically nothing is known about the early stages in the formation of smokes. Probably as in sols, the rate of nuclear formation and velocity of their growth are important stages. Now that it is realised that smokes originate from highly dispersed amicroscopic primaries there is hope that methods of attacking these difficult problems will be developed.

It will be obvious from the foregoing considerations that the experimental smokes so far discussed are special types. Although the particles composing them are aggregates and formed from a large number of primaries they are at least approximately homogeneous. This is evident from their appearance in the field of the ultra-microscope. Unfortunately no satisfactory quantitative studies have been made of the size distribution of particles in smokes. Both from the point of view of the theory of coagulation and also from that of the actual composition of smoke much is to be learnt from such investigations.

The ordinary smoke of factory and domestic chimneys and, indeed, the great majority of industrial and laboratory smokes belong to the heterogeneous type and exhibit a wide range in particle size forming frequently large loosely built aggregates of microscopic dimensions or irregular chains composed of small units. This structure which is characteristic of the particles in concentrated systems especially in

metallic oxide smokes must affect the mobility of the particles and their collision frequencies. Further, as Kohlschütter was the first to show the densities of such particles are very much smaller than that of the material composing them. Whether this structure revealed by the microscope is a replica on a larger scale of the structure of ultra-microscopic particles is an open question. The application of X-ray or electron diffraction methods to the examination of smoke films might here prove of considerable value and interest.

Up to the present no normal aerial systems have been discovered in which coagulation does not take place, and no counterpart to the sol stabilised by protective agents has been observed. Although the suspended particles in gases doubtless adsorb molecules of the medium, this effect appears to have little influence on their adhesion. It is possible that a stabilising action might be detectable in gases which are highly adsorbed by the disperse material. Again whether the particles carry electric charges or are electrically neutral has little affect on the rate of coagulation. It is well known that smoke particles readily catch ions of both signs from the surrounding medium and when formed in a highly ionised atmosphere, such as in the presence of X-rays or by high temperature reactions, are strongly charged, but the smokes contain as a rule equal numbers of + and - units and are usually electrically neutral. Highly charged unipolar smokes can, however, be formed and these might be expected to show a diminished rate of coagulation. This has been found by Fuchs to be the case for highly charged unipolar oil smoke, though experimental investigation is difficult on account of the space charge which quickly drives the particles to the walls of the containing vessel. In this investigation it is interesting to note that the splitting up of the complexes into simpler units was claimed to take place during charging.

The rate at which ions are caught by particles of various sizes and the limiting charge acquired in an ionic atmosphere of given intensity are important factors in electrical precipitation and will be discussed in communications to this meeting.

Apart from electrical precipitation which at the moment is probably the most practical way of removing fine particulate matter, a study of disperse systems in gases indicates the possibility of the development of other methods which may in the future have many applications. Theory indicates that the rate of coagulation is determined by the probability of encounter of particles in brownian motion. Any factor then, which will increase the sphere of influence or the mean free path of these smoke particles will hasten coagulation. The production of turbulence in the medium by the formation of eddies and vortices will bring this about to some extent though for fine particles it is not so effective as for larger.

Of great interest is the effect of sonic and supersonic waves in bringing about rapid coagulation. This has been studied both experimentally and theoretically in recent years, notably by Brandt and Hiedemann in Germany, and Andrade in this country, and striking results have been obtained.

The movements of smoke particles in a temperature gradient and the formation of a dust-free space around hot bodies has been known ever since the pioneering work of Aitken and of Lodge in the last century. Precipitation of smoke and dust on cold surfaces is a common phenomenon but the mechanism of the process and the forces involved has

never been satisfactorily explained. Attention has recently been turned to a more detailed study of this effect and it has been utilised on a small experimental scale in the thermal precipitator for determining dust and smoke in disperse systems in gases.

Dusts.

Whilst smokes are formed by condensation, dusts whether natural or artificial are produced invariably by disintegration or dispersion processes. Speaking generally they consist of larger particles which from their mode of origin are denser and composed of much larger units. Hence they sediment more rapidly than smokes. Again the number concentration in dust systems is usually low though on account of the size of the particles they reflect light and show a high optical density. Dusts do, however, coagulate and the large primary units stick together when they come in contact forming complexes, but the process is slow and plays only a secondary part in their life history. Theoretically the coagulation of these systems presents interesting features but it has not so far been studied in any detail. Another characteristic of dusts is the ease with which the particles acquire electric charges, probably produced by frictional effects. In combustible materials such as coal dust this easily leads to dust explosions when the medium is air.

The toxic effects of siliceous dusts in industry are well known, but although much careful work has been done in this field, information on what size ranges of particles are the most harmful is still scanty. Progress in the investigation of dusts, and indeed of all disperse systems in gases, is largely a question of technique. Until recently many methods used were open to criticism, but it is possible now to determine with accuracy the mass concentration, number concentration and size distribution in dusts. The investigations of Green have done much to advance this aspect of the subject.

In this brief survey emphasis has been laid on spontaneous coagulation as a specific characteristic of these systems. It must, however, be pointed out that the very dilute smoke which pollutes the air of cities, as well as the many natural systems included in the terms fog, mist, and haze, change only with extreme slowness on account of the low number concentration of their particles. Nevertheless, coagulation even in these systems may be of significance, especially in the case of atmospheric nuclei and very small particles.

PART 1 (a). THE GENERAL PROPERTIES OF DISPERSE SYSTEMS COMPOSED OF SOLID AND LIQUID NON-VOLATILE PARTICLES (i.e. SMOKE, DUST, OIL, FOGS, ETC.).

ON THE PROPERTIES OF AEROCOLLOID SYSTEMS, WITH REGARD TO THEIR DEPENDENCE ON THE METHODS OF FORMATION.

BY KARL ERNST STUMPF AND GERHART JANDER.

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Previous investigations have shown that in contrast with liquid sols, aerosols are invariably unstable systems which aggregate and sediment more or less rapidly. Hence the unstable condition of aerosols is only to be compared with the special case of the rapid coagulation of liquid sols.

In the investigation of aerosols, therefore, two important questions arise: (1) what properties do they possess in parallel with liquid sols, and (2) on what factors do the properties of aerocolloid systems depend. This paper will examine principally the problems associated with the second question.

The properties of liquid sols are determined mainly by (1) the nature of the dispersed material, (2) that of the dispersion medium, (3) the effect on the prepared sol of additions which influence the electrical charge of the disperse phase or exercise a protective colloid action, and (4) the method of preparation itself. We shall examine the extent to which the properties of aerocolloid systems are determined by these factors.

The aerosols hitherto investigated show real differences according to the chemical composition of the substance used. Thus mercuric iodide smokes and aerosols of certain dye stuffs¹ age specially rapidly, since the decrease in the number of particles and the increase in their size depend not merely on aggregation, but also on the isothermal distillation or sublimation taking place in these systems. These substances have an appreciable vapour pressure, which increases with increasing curvature of the surface,² i.e. with decreasing particle size, so that small particles evaporate more readily than large and the vapour condensing on the larger particles, still further increases their size.

However, in systems where isothermal distillation is absent, because of a vanishingly small vapour pressure, singularly rapid ageing has been observed, as in certain metallic oxide smokes,³ e.g. ferric oxide smoke.⁴ Whytlaw-Gray has shown that these systems aggregate in a special way with formation of chain-like aggregates. The individual particles possess to some extent a dipole nature; they unite preferentially at the surfaces of the individual particle, at which it would grow preferentially as a crystal.

¹ Whytlaw-Gray and Patterson, *Smoke*, London, 1932, 168 ff.

² W. Thomson, *Phil. Mag.* (4), 1871, 42, 448.

³ Whytlaw-Gray, *loc. cit.*, 51, 81 ff.

⁴ Jander and Winkel, *Kolloid-Z.*, 1933, 63, 5.

The formation of chain-like aggregates in aerosols also can depend on pyroelectric properties of the disperse phase. According to Beischer,⁵ the needle-like crystals of aminoazobenzene, produced by cooling the supersaturated vapour, are charged pyroelectrically in such a way that each end carries an opposite charge. Hence it is understandable that the smoke would aggregate rapidly, forming chains such as Beischer has observed ultramicroscopically. Moreover, even in the absence of isothermal distillation or any special kind of aggregation, the differences arising from the physical properties of the various substances used as aerosols also leads to more or less rapid ageing. The rapid coagulation of unidisperse sols may be described by Smoluchowski's equation in the form,

$$-\frac{dn}{dt} = \frac{2}{3} \cdot \frac{RT}{\eta N} \cdot n^2,$$

where $-\frac{dn}{dt}$ is the velocity of disappearance of n particles present at time t . R is the gas constant, T the absolute temperature, η the viscosity of the dispersion medium, and N the Avogadro number. In this simplified form, the equation holds good provided that the effective radius of the particle is equal to its real radius, *i.e.* provided that the particles remain attached to one another only at an actual collision. This law, which has been applied by Whytlaw-Gray⁶ to aerosols, presupposes spherical particles. This condition is fulfilled only in fogs or in smokes produced by cooling fogs if the solidifying droplet does not change its shape by crystallisation. The stearic acid smoke used by Whytlaw-Gray approximates to this ideal case. All smokes of substances difficult to melt or of readily crystallisable substances vary more or less widely from the above requirements, so that their more or less rapid ageing is understandable.

The properties of aerosols are, therefore, to a great extent dependent on the substance used.

So far as we know, no investigations have been made of the effect of the gaseous dispersion medium on the resulting colloid system. From Smoluchowski's equation, we should expect the viscosity of the medium to affect the coagulation velocity, in the sense that the velocity increases with decreasing viscosity.

Attempts to influence the behaviour of the prepared aerosol by electrification, or by the addition of "protective" substances, clearly show the great difference between liquid sols and aerocolloid systems. This is due to the difference in the dispersion medium, liquid or gas. Both in lyophobic and in lyophilic sols, the dispersion medium plays an important part in stabilising the sol, by making unipolar electrification possible or by adsorption at the surface of the particle. Whytlaw-Gray and his co-workers⁷ and others⁸ have nowhere indicated any such stabilising action of the dispersion medium on aerosols. At the slight degree of electrification, bipolar or unipolar, which certain methods of preparation produce, no measurable effect on the rate of ageing has been detected. Moreover, with the usual strong unipolar electrification, no stabilisation results. There must be other effects, unknown in liquid sols, which permit the disappearance of aerosols. N. Fuchs has shown recently⁹ that strongly

⁵ *Z. physik. Chem. A.*, 1930, **176**, 1.

⁶ *Loc. cit.*, 57 ff.

⁷ G. Jander and A. Winkel,⁴ 10 ff.

⁸ N. Fuchs and J. Petrijanow, *Acta Physicoch. U.R.S.S.*, 1935, **3**, 827.

⁹ *Loc. cit.*, 146 ff.

charged unipolar aerosols do not aggregate, as might be expected, owing to the electrical repulsion between the particles; however, the cloud has a tendency to expand. The particles migrate to the walls of the vessel, to which they give up their charges and remain attached. Stabilisation would be obtained by unipolar electrification only if the walls of the vessel were charged, and of the same sign as the charges on the particles, so that the tendency of the particles to migrate to the walls would be compensated by the repulsion exerted on them by the correspondingly charged walls.

By analogy with liquid sols, stabilisation of aerosols by the action of protective colloids is conceivable, so long as these protective aerosols are stable as pure aerosols, *i.e.* so long as they do not aggregate on undergoing the collisions due to their Brownian motion, but collide elastically. Such aerosols are at present unknown; the majority of collisions between particles lead to aggregation. Aggregation may, however, be retarded by the addition of substances which are adsorbed at the surface of the particles,¹⁰ an effect certainly not due to elastic collisions between the protected particles. Probably the effect is to be ascribed to impedance of factors which accelerate ageing, such as isothermal distillation, or the formation of polar crystalline particles. The stabilising substances so far used (*e.g.* phenol or oleic acid) cannot be added subsequent to formation of the aerosol, but must be evaporated along with the substance forming the sol, so that they condense with it. No experiments (particularly with regard to a possibly expected retardation of the coagulation velocity) have been made with subsequent additions of vapour to be adsorbed as a protective envelope.¹¹ So far, then, attempts to stabilise aerosols, either by electrification subsequent to preparation, or by the addition of other substances, have achieved no real success.

In contrast with liquid sols, therefore, the properties of a given aerocolloid system are fixed as soon as its preparation is complete. Of the more important methods of preparation, the first comprises the subdivision of a coarser system * to one of particles of colloidal dimensions. The second method involves producing a colloidal disperse phase by aggregation or coagulation from a molecularly disperse (gaseous) phase. All the usual methods of preparation depend on this condensation process methods. It may be further subdivided into three groups, the physical, chemical and photochemical condensation methods.¹²

In the physical condensation method, the substance to be investigated is heated to produce evaporation of a considerable mass and the disperse colloid phase results by subsequent condensation. In this way, aerosols of a large number of inorganic and organic substances have been prepared.

By chemical condensation methods, two substances in the form of vapour react with the formation of a product, whose vapour pressure at ordinary temperatures is very slight, or practically zero (*e.g.* NH_4Cl smoke from HCl and NH_3 ; H_2SO_4 fog from SO_2 and steam and metallic oxide smokes from zinc ethyl or from base metals evaporated in the arc with atmospheric oxygen).

By the photochemical condensation method, a substance suitably illuminated yields an aerosol product of vanishingly low vapour pressure. So far, only ferric oxide dusts, resulting from the photochemical decomposition of iron pentacarbonyl, have been obtained by this method.⁴

In order to obtain reasonably reproducible results, it was necessary to improve the methods of preparation of aerosols. Using a physical conden-

¹⁰ A. Winkel and G. Jander, *Schwebstoffe in Gasen*, Stuttgart, 1934, 43.

¹¹ H. Remy, *Z. angew. Chem.*, 1933, 46, 610, and earlier papers; A. Krassilchikov, *Kolloid Z.*, 1936, 74, 138.

* The atomisation of liquids is the outstanding example, and is unimportant since only relatively coarse, rapidly aggregating polydisperse systems are obtained. It is excluded, therefore, from consideration.

¹² V. N. Fuchs, *Über die Bildung von Aerosolen*; *Acta Physicoch.*, U.R.S.S., 1935, 3, 61.

sation method, Whytlaw-Gray¹² succeeded in preparing highly reproducible aerosols, especially of stearic acid, by using a constant weight of the fog-forming substance and carefully maintaining every detail in the preparation unchanged, otherwise aerosols of different behaviour resulted. The substance was heated in a stream of air in an electrically-heated boat, and the vapour-charged air stream was rapidly cooled by dilution with the cold air in the chamber. If the substance was evaporated directly into the chamber and distributed by stirring, the resulting aerosols at once coagulated more rapidly to much coarser systems, a method which is less exact and yields only poorly reproducible aerosols.

With chemical condensation methods also, finely divided, reproducible aerosols cannot be obtained if the gaseous reactants are mixed directly in the chamber. Fuchs and Oschman¹⁴ have, however, prepared very finely divided and highly reproducible fogs from sulphur trioxide and air containing water vapour, by greatly diluting the reactants and allowing them to react after thorough mixing (by the method they describe) before introduction and distribution through the chamber; the system is rapidly diluted to the concentration at which the investigation is carried out, perhaps simultaneously with the completion of condensation and the beginning of coagulation. This method is only suitable, however, for the production of finely divided and very dilute fogs. Whytlaw-Gray has shown that the electric arc as a means of preparing smokes under reproducible conditions is still less suitable.¹⁵ In contrast to those prepared by other methods, aerosols prepared by the arc are mainly charged and of both signs and, moreover, the formation of chain-like aggregates is clearly shown, a property due more to the nature of the metallic oxide than to the method of preparation.

The ferric oxide dusts⁴ prepared by the photochemical condensation method are exceptionally finely divided and highly stable sols with extreme reproducibility.

The most finely divided and most stable systems (and the most reproducible) result by using methods in which the condensation proceeds under the most uniform conditions, and the freshly formed very finely divided aerosol can be equally rapidly and uniformly distributed through the chamber; they age more slowly than aerosols prepared in other ways. According to Müller's theoretical treatment of hydrosols,¹⁶ polydisperse systems coagulate more rapidly than unidisperse systems of the same concentration and particulate number. Approximation to complete unidispersity can only be realised in the very earliest stages, since with the onset of aggregation the condition of uniformity is immediately destroyed. For all quantitative investigations, therefore, it is simpler to use systems which are as unidisperse as possible.

To obtain reproducible, unidisperse systems, special attention must be paid to the conditions under which condensation and coagulation up to the time of uniform distribution in the chamber take place. Our knowledge of the course of these two important processes is slight. Scarcely any work has been carried out apart from investigations on water fogs,¹⁷ on the rôle played in condensation by condensation centres and foreign nuclei. According to Whytlaw-Gray's views,¹⁸ for substances of very low vapour pressure, like stearic acid and arsenic, so high a degree of supersaturation will be produced that the molecules of the vapour itself become effective centres for condensation, so that no foreign nuclei need to be assumed. This will only be the case, however, if the cooling and consequent

¹² *Loc. cit.*, 44.

¹⁴ *Acta Physicoch.*, U.R.S.S., 1935, 3, 65.

¹⁵ *Loc. cit.*, 76, 77.

¹⁶ Wiegner and Tuorila, *Koll-Zeitschr.*, 1926, 38, 3.

¹⁷ See Freundlich, *Kapillarchemie*, 4 Aufl., 1932, 2 Bd. 780 ff.

¹⁸ *Loc. cit.*, 74 ff.

high supersaturation are accomplished rapidly. Now, the cooling of the vapour takes time, and proceeds through all stages from saturated vapour to a state of high supersaturation. At the beginning of condensation, the larger foreign nuclei will act as centres at which larger aerosol particles will be formed. In time, greater supersaturation will ensue, and in addition to the larger particles already present, smaller particles will be formed with the molecules of the substance itself acting as condensation centres. Thus the kind of cooling (*Abschreckung*) will exercise a profound influence on the nature of the aerosol. The faster the cooling, the faster will the critical region (in which larger particles are formed at foreign nuclei) be passed through, leading to a correspondingly more finely divided and uniform aerosol. In the chemical and photochemical condensation methods, the "chilling" is instantaneous, and hence the magnitude of the supersaturation depends on the speed of the reaction.

Moreover, even in respect of the coagulation which occurs prior to distribution in the chamber, rapid cooling of the condensing vapour is valuable. From Smoluchowski's equation describing the course of coagulation given above we may deduce the effect of temperature, viscosity of the medium and particle concentration on the rate of coagulation. The higher the temperature and the higher the particle concentration, the more rapidly will the aerosol age. If, therefore, cooling is effected slowly, aggregation to coarser particles will proceed proportionately rapidly. The original concentration of the vapour to be condensed similarly influences the aerosol produced; the higher the vapour concentration, the higher the concentration of the resulting aerosol, and the more rapidly will it aggregate. This explains why direct evaporation in the chamber and distribution of the vapour by mere stirring results in coarse heterogeneous systems. In this case, the density of vapour is high at the start, the cooling is in no way uniform and relatively very slow, whereas, if the substance is heated in a tube and blown into the chamber, the vapour and the aerosol concentrations are low, so that by the more rapid and more uniform cooling, a more unidisperse system is distributed through the chamber by the stirring apparatus. Reproducible results can, therefore, be obtained by accurate control of the temperature of heating, velocity of the air stream and rate of stirring in the chamber. Reproducibility is also related to the amount of substance dispersed as fog, in that at the same temperature, a correspondingly longer time is required for the evaporation of a larger amount of material. As a result, whilst the last portions of the substance are evaporated, the earlier portions are already distributed throughout the chamber as aerosol to which the small primary particles rapidly unite with particles which are already aggregated. This explains why arsenic dusts prepared under the same conditions showed different behaviour according to the concentration.¹⁹

Fig. 1, taken from the paper cited, shows that the more concentrated systems are actually more polydisperse than the more dilute systems. Owing to the longer time needed for the preparation, the final portion evaporated, condenses and aggregates on the particles first formed. By the rapid sedimentation of the large particles thus formed, the average weight of the particle at first quickly falls, until a finely divided and homogeneous system remains; it then begins to rise as expected, owing to coagulation. Since the more dilute systems, owing to their shorter time of preparation, are already uniform, the change of particle weight with time is as expected from the start.

In addition to the condensation and initial coagulation at greater concentrations, the method of distribution in the chamber is of importance in securing uniformity in the resulting system, otherwise imperfect results are obtained. Even when the formation of the aerosol is practically complete before its entry into the chamber, uniform distribution, to which

¹⁹ G. Jander and A. Winkel, *Kolloid-Z.*, 1933, 65, 290.

stirring contributes, opposes homogeneity in the particle size, despite the most careful experimental conditions. This can be roughly confirmed by first distributing the vapour uniformly in the experimental vessel and then effecting sudden condensation, either by cooling or by adiabatic expansion. Condensation invariably occurs partly in the concentrated vapour and partly only during the final distribution in the chamber. Thus, aggregation occurs at different concentrations until uniform distribution has been secured, so that it is never possible to achieve more than approximate homogeneity and reproducibility.

The same state of affairs arises with the chemical condensation methods. If the reactants are first mixed in the chamber, a heterogeneous, rapidly coagulating aerosol results. It is only when the reaction is practically completed before the mixture enters the chamber under constant conditions that highly reproducible fogs are obtained, as Fuchs¹⁴ has shown.

The degree of uniformity secured by the methods so far used depends on the extent to which it is possible to direct and influence reproducibly, the condensation process and the coagulation occurring in the short time prior to entry into the chamber. This cannot be done rigorously, since

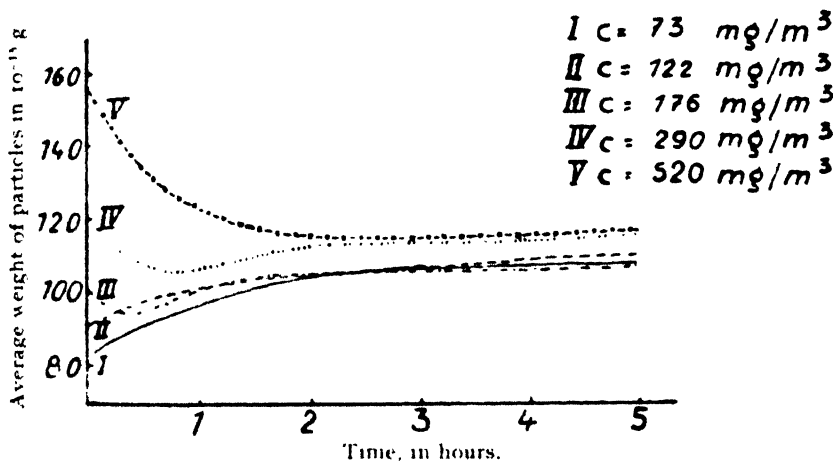


FIG. 1.

the two processes follow one another with differences of time and place. The systems thus result from a complex procedure, and must themselves be more or less complex in nature.

We believe that the photochemical method of preparing ferric oxide smokes, should, at least in principle, avoid some of the complications arising in the previous methods. For example, the iron pentacarbonyl from which the aerosol is generated, may be uniformly distributed through the vessel as a vapour. With uniform and intense irradiation by ultra violet light, the formation of the aerosol may be accomplished uniformly throughout the entire volume, and hence the circumstances of condensation and coagulation are everywhere the same. The stirring, essential in other methods to obtain uniformity of distribution, must accelerate coagulation, and is practically dispensed with in this method. We are therefore able with certainty to produce as uniform an aerosol as possible. With sufficiently powerful illumination, strictly comparable aerosols of different concentrations can be prepared. Whilst arsenic dusts prepared thermally and under the same conditions deviated widely from one another in behaviour, according to their concentration, Fig. 2 shows that ferric oxide smokes of different concentration are not so differentiated; the decrease in concentration and in number of particles are always in the same sense.

The two series of experiments cannot be strictly compared unrestrictedly, because of the different ranges of concentration. The smaller initial average weight of particle in the ferric oxide smokes, in comparison with that of the arsenic smokes, is characteristic of a highly undisperse aerosol.

Whytlaw-Gray²⁰ has shown that ferric oxide smokes are not, unfortunately, suitable for general investigations, as they aggregate in a special way. Moreover, the course of the reaction expressed by the equation



is completely unknown, so that unforeseen complications may arise here.

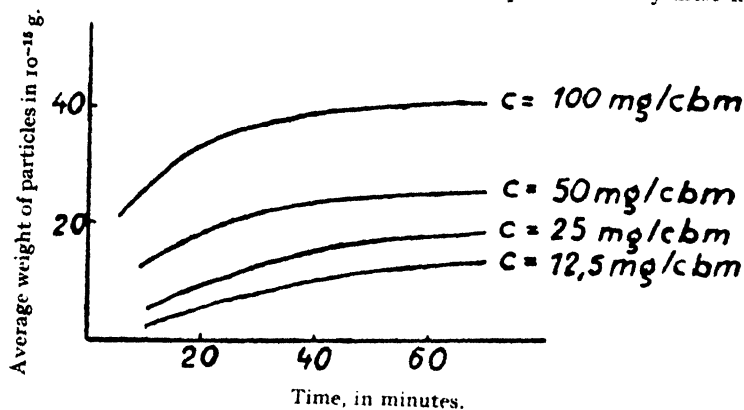


FIG. 2.

Summary.

The behaviour of an aerosol will be decisively affected by the chemical and physical conditions prevailing during preparation, particularly in regard to the form and size of the particles formed. Relatively finely divided and approximately undisperse systems have been obtained in different and reproducible ways, in all of which, however, there are some imperfections, which have been discussed. No method of preparation, ideal in every respect, has so far been evolved. Further improvement in methods of preparation depending on a closer knowledge of the rapidly occurring process of condensation preceding the formation of particles of colloidal dimensions, seems to us important, if we are to penetrate further into the characteristics of aerosols.

²⁰ Whytlaw-Gray, *J. Chem. Soc.*, 1935, 276.

GENERAL DISCUSSION.

Dr. N. Fuchs (Moscow) (communicated): In the work of Urasovski and Kusmenko,¹ the dispersity of NH_4Cl smokes formed by volatilisation in different media was compared, the number of particles per c.c. in 30-minute old smokes being

Medium.	Air.	Methane.	Methyl Alcohol.	Ethyl Alcohol.	Propyl Alcohol.	Benzene.
Number of particles per c.cm.	1.0×10^6	1.5×10^6	2.5×10^6	3.0×10^6	0.5×10^7	0.8×10^7

¹ Urasovski and Kusmenko, *J. Physic. Chem.* (Russian), 1935, 6, 896.

As the weight concentration of smokes was very large (2 grams per cubic meter) they must have been very highly coagulated by the time they were examined and the results obtained can be interpreted as due chiefly to the different rate of coagulation in these media. The above figures show a complete parallelism with the diffusion coefficients of the media.

The same authors studied also the effect on the dispersity of smokes caused by the small admixture of some easily adsorbed vapours to the air in which they are formed. Only highly coagulated smokes were again examined. The most striking effect was observed with the admixture of phenol vapours, which markedly increased the dispersity of some smokes (NH_4Cl) and decreased that of others (MgO). We agree completely with Stumpf and Jander that this effect should not be attributed to the change in the effectiveness of collisions between the particles caused by the adsorbed layer. Most likely this layer causes a change in the size and form of the primary crystals,* and consequently in the structure of the aggregates formed from them. It would be very desirable to repeat these experiments, but adding the phenol vapours not before but after the formation of the smoke, as Stumpf and Jander have quite justly remarked.

The charging of the walls of the smoke-chamber (p. 1050) will not lead to any stabilisation of an unipolarly charged smoke. If all the walls are charged to the same potential there will be no field whatsoever inside the chamber. If the potential is different—the particles will move across the chamber and settle on one of its walls.

* Cf. crystallisation from solutions.

A SEDIMENTATION METHOD OF FINDING THE NUMBER OF PARTICLES IN SMOKES.

BY R. WHYTLAW-GRAY, W. CAWOOD AND H. S. PATTERSON.

Received 10th February, 1936.

The interpretation of the process of coagulation in smokes which has been previously put forward¹ depends upon the accuracy of counting in an ultramicroscope cell. We have shown that the Zsigmondy slit ultramicroscope gives an entirely erroneous estimate of the number of particles, and in consequence a special type of cell which we believe enables accurate data to be obtained was developed and used.² The unreliability of the slit ultramicroscope was first revealed by preliminary experiments on the sedimentation of smokes. This sedimentation method has been perfected and since it is free from certain objections which might be urged against counting with the special cell, the agreement which we have found serves to conform the validity of the previous conclusions on smoke coagulation.

Essentially the method consists in enclosing a known volume of smoke taken from the centre of the experimental smoke chamber between two strips of optically worked glass which form the top and bottom of a shallow box. The particles settle mainly on the lower plate and the number of particles can be counted when the deposit is suitably illuminated. Knowing the depth of the box and the area in which the count is made, it is easy to calculate the number of particles per c.c. of the smoke.

¹ Patterson and Cawood, *Proc. Roy. Soc.*, 1932, 136A, 538.

² Nonhebel, Colvin, Patterson and Whytlaw-Gray, *Proc. Roy. Soc.*, 1927 116A, 540; Patterson, Whytlaw-Gray and Cawood, *ibid.*, 1929, 124A, 502.

Sedimentation Method of Counting.

The enclosing of a known volume of smoke was accomplished by means of the device shown in Fig. 1.

The two glass plates A and B slide along the surface of a brass plate C perforated with a hole G. The glass plates are kept in position by sliding in grooves D, and are raised slightly above the level of the brass plate by strips of paper gummed to their edges. This device prevents abrasion of the highly polished surfaces by the brass. To the top of the plates are gummed strips of thin velvet ribbon to ensure that the plates fit tightly and move smoothly in the grooves. The plates originally occupy the position EF and are pulled simultaneously over the aperture into the position HK by means of strings. The small volume of smoke present in G is thus enclosed between the two glass plates and in standing sediments almost entirely on to the lower. The plates used are about

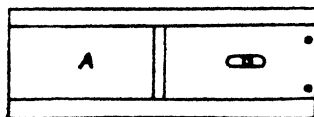
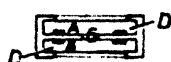


FIG. 1.

9 cm. long by 3 cm. wide with a bevel at the front end whilst the aperture G is oval, the size being about 1.2 cm. by 2.5 cm. Owing to slight turbulence and to diffusion, the deposit is apt to be irregular near the edges and it is therefore necessary that the area of G shall be large. In practice, however, the greater part of the deposit is perfectly uniform provided that the cell is not too deep. Actually, we have used cells varying in depth from 2 to 10 mm. and within these limits the deposit is quite satisfactory though it is more uniform the shallower the hole. The brass holder carrying the plates was designedly of heavy metal to ensure thermal equilibrium and the absence of convection in the smoke during settling. We have termed the glass plates collector slides, and the brass cases in which they slide, collector slide holders.

After the deposit had settled, the slides were removed from the holder and examined microscopically, using a 16 mm. apochromatic objective N.A. 0.30 and a ($\times 12$) or ($\times 20$) eyepiece carrying a suitable squared graticule. The surface of the slide on which the particles had sedimented was illuminated from the front by a powerful focused beam of oblique light. The particles thus appeared as small bright diffraction discs on a black background. These operations were always carried out in a dust-proof box containing the microscope and slides, to avoid errors due to the deposition of floating impurities in the air. Counting presented no difficulty, the average number of particles per square of the eyepiece being obtained by enumerating a large number of fields in different parts of the deposit. Knowing the number of particles per square, the area of slide corresponding to the square, and the depth of the slide, the number of particles per c.c. can easily be found.

In the intense beam of illumination used the ordinary surface of glass even when optically polished shows numerous imperfections which simulate particles. By special polishing however, these can be almost entirely eliminated. In addition it is necessary that the surfaces before use shall be carefully cleaned. With certain types of glass this cleaning is not very difficult when the technique has been acquired and the surface when cleaned remains free from imperfections over long periods. With other

types of glass it appears practically impossible to rid the surface, even for short periods, of particulate matter. Thus on one hand the gentle friction of cleaning may produce such electrification of the surface that any particulate matter in the vicinity descends on the slides like a snow-storm, whilst on the other, particulate films due probably to moisture, may be almost impossible to eliminate or may be formed on standing for a short period. We wish to express our indebtedness to Sir Herbert Jackson, K.B.E., F.R.S., for kindly advising us as to the best types of glass to use, and also to Messrs. Hilger, Messrs Taylor, Taylor and Hobson, and Messrs. Cooke, Troughton and Sims, for obtaining the very special surfaces necessary. Even under the best conditions, however, the cleaning of the slides calls for considerable skill. In all cases when the slides had been cleaned, they were examined before use in the manner described to ensure that they were free from deposits. Also after they had been exposed to a particulate cloud, the unexposed portion was scrutinised to see that the surface had not deteriorated. We found that the cleaning was best effected by a fine lawn cloth which had been treated beforehand with hot sodium carbonate solution and washed in pure water. The slightest trace of grease spoilt the surface immediately.

In studying the coagulation of a smoke, six or more of these collector slides were fixed to a suitable support in the centre of the smoke chamber and the slides were drawn at definite times by means of strings passing through corks in the side of the chamber.

Experimental Results for Coagulation.

This method has been applied to a large number of smokes and a considerable mass of data accumulated. A few typical results giving the

TABLE I.

Cadmium Oxide.			Cadmium Oxide.		
Time from Start, Min.	Number per c.c. $\times 10^{-6}$.	Particulate Volume $\times 10^7$	Time from Start, Min.	Number per c.c. $\times 10^{-6}$.	Particulate Vol
3	2.95	3.30	2	5.37	1.86
7	1.70	5.88	5	2.41	4.15
11.5	1.14	8.81	10	1.59	6.29
19.5	0.778	12.85	20	0.696	14.4
26.5	0.571	17.50	25	0.671	14.9
40.5	0.425	23.55	30	0.628	15.9
49.5	0.385	26.00	35	0.482	20.8
60	0.322	31.10	45	0.387	25.8
102	0.174	57.5	55	0.303	33.0

variation of number and particulate volume with time are given in Table I. The corresponding particulate volume-time curves are shown in Fig. 2.

It is evident that these coagulation curves are entirely analogous to those obtained with the special ultramicroscope cell. Actually a number of comparisons of two methods of counting have been made simultaneously on the same smoke. For this purpose, cadmium oxide smoke from a cadmium arc was used. The data obtained in two different experiments are given in Table II., whilst Fig. 3 shows the corresponding particulate volume-time curves.

It will be seen that there is a close agreement between the two sets of results. This is, perhaps, the more striking when it is considered that

the two methods are subject to entirely

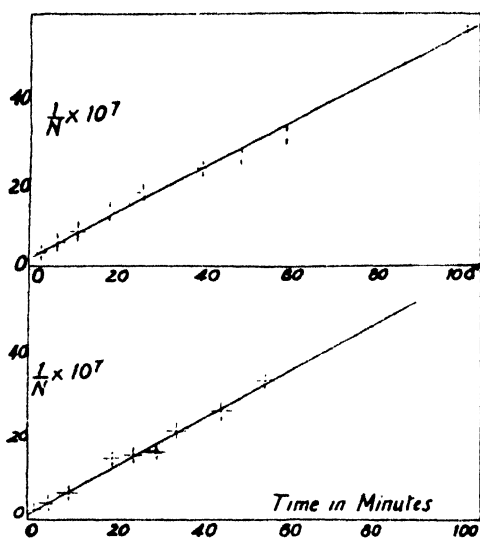


FIG. 2.

different errors. It may be remarked that the examples given are those for smokes of a heterogeneous type which exhibit a large variability in the coagulation rates.

Counting by sedimentation has, however, its limitations. It is essential that the material used shall not be hygroscopic and obviously liquid particles which tend to wet the glass cannot be counted after settling on a slide. We have often watched the settling of tobacco smoke, of which a number of the particles are liquid, on a glass surface and it is interesting to see how rapidly the majority of the particles either disappear or diminish greatly in brightness when they come into contact with the glass. Further with a highly dis-

TABLE II.

Counts with Cell.			Counts with Collector Slides.		
Time from Start in Minutes.	Number per c.c. $\times 10^{-4}$.	Particulate Volume $\times 10^7$.	Time from Start in Minutes.	Number per c.c. $\times 10^{-4}$.	Particulate Volume $\times 10^7$.
Experiment I.					
10	1.10	9.1	20.5	0.61	16.4
16	0.758	13.2	30.5	0.49	20.4
23.5	0.654	15.3	42.0	0.42	23.8
28	0.529	18.9	55.5	0.33	30.3
39	0.439	22.8	73.0	0.29	34.5
45.5	0.418	23.9			
50	0.372	26.9			
58	0.320	31.3			
62	0.325	30.8			
71	0.248	40.3			
86	0.230	43.5			
90	0.213	46.9			
Experiment II.					
7	0.909	11.0	8	0.92	10.9
12	0.990	10.1	24	0.47	21.3
17	0.629	15.9	43	0.33	30.3
22	0.553	18.1	62	0.24	41.7
27	0.481	20.8	84	0.21	47.6
31	0.412	24.3			
39	0.337	29.7			
46	0.345	29.0			
59	0.295	33.9			
73	0.218	45.8			
82	0.198	50.5			
95	0.168	59.4			
101	0.181	56.4			

perse smoke, especially in its early stages, all the particles may not be enumerated on account of the low intensity of the light scattered by the smaller units. In addition, a time correction of small but uncertain magnitude should be applied to these early points to allow for the coagulation taking place during sedimentation. Consequently, the collector slide counts for very fine smokes will be too low.

GENERAL DISCUSSION.

Dr. R. Lessing (*London*) asked whether the method was also applicable to dusts.

Professor F. G. Donnan (*London*) drew attention to the fact that the first observations on photochemically produced disperse systems in gases were made by Tyndall very many years ago. In fact, the famous "Tyndall beam" arose from this work.

Dr. F. T. Peirce (*Manchester*) said: The question seems to be whether there is real physical meaning in the zero of time on the coagulation curve. Is the extrapolation to zero made along the linear empirical relation of $1/n - t$, or in accordance with the theoretical expression for K ?

Dr. W. Cawood (*Leeds*), in reply, said: The method would be easily applicable to dusts of the size range down to the limits given. We have successfully obtained a thick deposit with dusts of low concentration, by using collected slides of greater depth than those described. This method is, of course, quite different from the ordinary method of sedimentation on to a cover glass, where the glass surfaces are not sufficiently perfect for oblique illumination to be used and with direct light the smallest particles are not counted.

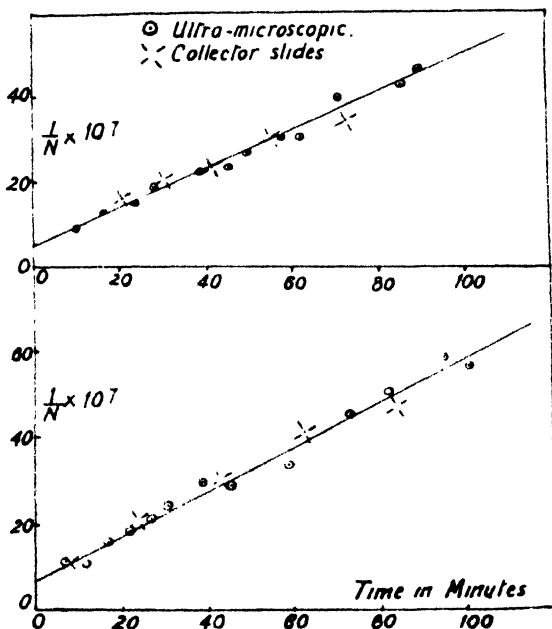


FIG. 3.

THE INFLUENCE OF PRESSURE ON THE COAGULATION OF FERRIC OXIDE SMOKES.

BY W. CAWOOD AND R. WHYTLAW-GRAY.

Jander and Winkel,¹ in a comprehensive research on ferric oxide aerosols, have shown that perfectly reproducible smokes can be obtained by the photochemical decomposition of dilute iron carbonyl vapour ($\text{Fe}(\text{CO})_5$) in air. They point out that these ferric oxide smokes exhibit, in their early stages at least, a high degree of homogeneity and that the

¹ *Kolloid Z.*, 1933, 63, 5.

method provides a ready means of studying the coagulation of aerosols at varying pressures.

The results, however, which they obtained for the course of coagulation at atmospheric pressure differ markedly from those of the majority of smokes we have examined and we attribute this difference to the method employed for counting the number of particles. Moreover, the experiments they carried out at pressures below atmospheric, though showing clearly that coagulation takes place at a greater rate, did not give any indication of the form of the coagulation curves. For these reasons a further study has been made of the ferric oxide aerosols which are formed by the very elegant method of photochemical decomposition discovered by these two investigators.

Experimental.

In any research on the coagulation of smokes the essential measurement is the determination of the change with time of the number of particles per unit volume. For this purpose counting with the Zsigmondy slit ultramicroscope is often used, but this method, as we have shown, is unreliable when applied to smokes and may frequently lead to erroneous results.² In the experiments to be described we have therefore used the improved form of counting cell and the method which experience has shown to be reliable.³

Our arrangements have been criticised by Jander and Winkel⁴ but we wish to point out that our method has been tested by comparison with two other independent methods of counting, *viz.*: the modified Aitken method developed by Green⁵ and a sedimentation method described in this discussion. All three methods agree closely. We believe, therefore, that our system of counting particles is reliable.

The smokes were dispersed in a similar manner to that used by Jander and Winkel.¹ A thin glass capsule containing a solution of iron carbonyl dissolved in anhydrous ether was broken by means of an electromagnetic arrangement, at the centre of a 20 litre pyrex globe containing filtered air. The flask was radiated by placing it upon a rotating table between two 10 ampere arcs for six minutes. It was then connected with the counting cell and observations were made at suitable intervals of time.

The first experiments were carried out at atmospheric pressure, in order to test the reproducibility of the smokes. Three smokes of equal weight concentrations (16.5 mgms. Fe_2O_3 per cubic metre) were counted. When the results were plotted in the usual manner of particulate volume against time, straight lines were obtained in each case, within the limits of experimental error. Plotted in this manner each graph extrapolated back to near the origin and the slopes of the three agreed closely, the

following values for the coagulation constant K in the equation $\frac{1}{n} - \frac{1}{n_0} = Kt$ being obtained.

Concentration.			K . (cm. ³ /min. $\times 10^3$).
1.	16.5 mgms.	per cubic metre	0.408
2.	"	" "	0.407
3.	"	" "	0.399

The experimental points of one of the smokes are reproduced in Fig. 1. These results show that the smokes are highly reproducible, and that

² *Proc. Roy. Soc.*, A1927, 116, 540.

³ Patterson, Whytlaw-Gray and Cawood, *Proc. Roy. Soc.*, A1929, 124, 502.

⁴ *Schwebstoffe in Gasen*, 1934, pp. 16 and 44.

⁵ *Phil. Mag.*, 1927, 4, 1046.

the coagulation curves are very similar to those which we have obtained previously. They do not, however, agree with Jander and Winkel's graphs for smokes of a similar concentration, which exhibit a distinct curvature and show a much higher number concentration at corresponding times. It may be noted that earlier counts made by one of us with a Zsigmondy slit ultramicroscope and known to be erroneous, approximate closely to their results.*

Coagulation curves at pressures below atmospheric were obtained in the following way. After filling the 20 litre globe with filtered air and introducing the thin glass capsule containing the ethereal solution of iron carbonyl of the standard concentration, the pressure was reduced to a suitable value. The capsule was then broken and the flask radiated. Coagulation was allowed to proceed for a definite period and then filtered air was admitted until atmospheric pressure was reached. The smoke was then thoroughly mixed and counts taken in the usual manner over a period of about half an hour. The extrapolation of the graph so obtained back to the time when the air was admitted gave the number of particles per c.c. to which the smoke had coagulated at the reduced pressure. This procedure was carried out a number of times at the same initial pressure, allowing different

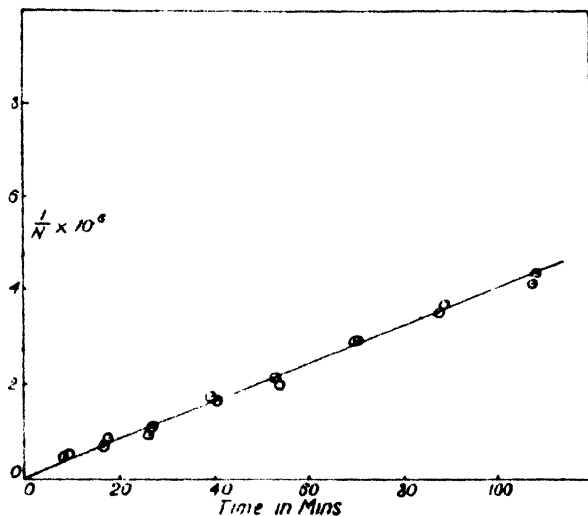


FIG. 1.

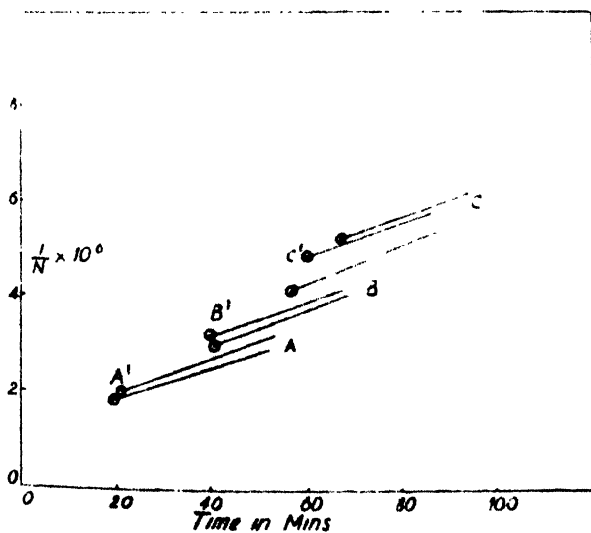


FIG. 2.

intervals to elapse before the pressure in the flask was brought up to atmospheric. In this way a number of points was obtained on the coagulation curve at the low pressure. The accuracy of this method

* *Proc. Roy. Soc., A* 1922, 102, 601

depends upon the degree of reproducibility of the smokes, but the data obtained from different experiments were perfectly consistent and showed no indication of irregularity. The method will be clear from Fig. 2. Thus the lines A, B and C represent the experimental graphs obtained after letting air into the globe. These all proved to be straight lines

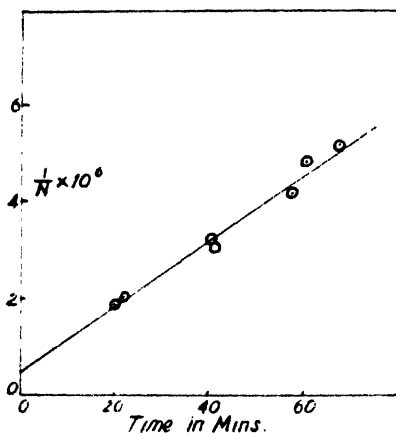


FIG. 3.

parallel to the coagulation graph at atmospheric pressure. A^1 , B^1 and C^1 are the points obtained by extrapolating the experimental graphs back to the time when the pressure in the flask was brought to atmospheric. It may be noted that there is very little error in this as the extrapolation is only of the order of two or three minutes. The points A^1 , B^1 , and C^1 were then plotted as in Fig. 3, showing the course of the coagulation at the lower pressure. The actual points plotted in Figs. 2 and 3 correspond to the results taken at 400 mm. pressure. The graph at 200 mm. pressure was obtained in a precisely similar manner. In Fig. 4 are reproduced the coagulation curves at 760 mm., 400 mm. and 200 mm. pressure.

These experimental graphs show several interesting features. They confirm Jander and Winkel's observations that the rate of coagulation increases markedly as the gas pressure falls. On the other hand, the relationship between the number of particles present after the same interval of time in systems coagulating at different pressures does not, as these observers affirm, appear to vary linearly with pressure.

The graphs, over the time range considered, are straight and when extrapolated to zero time do not start from the same point. This would indicate that at the lower pressure a smaller number of particles is formed initially than at the higher pressures. With stearic acid it has been shown⁶ that in air at normal pressure the number of primary particles must be very large and of the order of 10^{13} per c.c. This

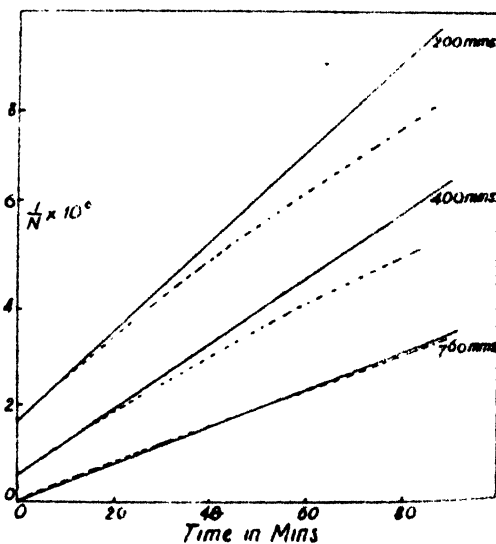


FIG. 4.

value is in approximate agreement with a direct experimental determination made by Fuchs and Oschman,⁷ in which they found the initial number per c.c. about 10^{13} and the radius 1.2 to 1.5 10^{-6} cm. in a sulphuric acid aerosol at atmospheric pressure.

Our graphs for Fe_2O_3 at atmospheric pressure also indicate a very

⁷ *Acta. Physica chimica U.R.S.S.*, 1935, III, 61.

high initial number and consequently a small value for the radius of the primary particle, whilst those for the 200 mm. pressure show that coagulation must start from much larger units.

Although little is known directly about the early stages of smoke formation it is probable that nuclei are first formed in the supersaturated vapour and that a proportion of these grow rapidly by condensation to primary particles. On this view the results we have obtained indicate either that the number of nuclei present in the initial stages changes rapidly with pressure, or that the number of nuclei is constant but the proportion developing into primary particles becomes smaller as the air pressure falls. The particles in the Fe_2O_3 smokes formed at atmospheric pressure should hence consist of aggregates of amicroscopic or ultra-microscopic primaries whilst those formed at low pressures should be composed of markedly coarser units.

To test this point a microscopic examination was made of the deposits obtained from two ferric oxide smokes of the same weight concentration, one of which had been formed and allowed to coagulate for three hours at atmospheric and the other at a pressure of 200 mm. The deposits were obtained both by direct sedimentation on to microscope cover slips and by thermal precipitation. They were examined with a 2 mm. Leitz apochromatic oil immersion objective and illuminated by transmitted light of short wave-length. A marked difference in the character of the units composing the aggregates was at once apparent. In both cases chain-like complexes were predominant but the units in those formed at the higher pressure were beyond the limit of microscopic resolution and were indeed extraordinarily difficult to observe at all, whilst those in the aggregates formed at the lower pressure were very distinctly larger and easily observable.

This result confirms in an entirely satisfactory manner the explanation given of the different starting-points of the graphs in Fig. 4. The effect of gas pressure on the size of the particles is also supported by results obtained by Kohlschutter with smokes of metallic oxides dispersed from an arc in air at various pressures.⁶

The general form of the three graphs and their theoretical significance now calls for some discussion.

Discussion.

It has been shown that the coagulation of various types of smoke is in conformity with the theoretical expression of Smoluchowski, if certain modifications are inserted to take account of the heterogeneity and the mobility of the smoke particles.³ Thus the coagulation of a smoke containing about equal numbers of particles of range of radius of about 1 to 7 is given by

$$-\frac{dn}{dt} = \frac{4RT}{3\eta N} \left(1 + \frac{Al}{r}\right) \times 1.25, \quad \text{where } n = \text{number of particles per c.c.,}$$

$n_0 = \text{initial number of particles per c.c.,}$

$l = \text{mean free path,}$

$r = \text{radii of particles,}$

$\eta = \text{viscosity of gas.}$

and consequently

$$t = \frac{\sigma - \sigma_0}{\frac{4RT}{3\eta N} \left(1 + \frac{Al}{r}\right) 1.25} \quad \sigma = \frac{1}{n},$$

$$\sigma_0 = \frac{1}{n_0}.$$

⁶ Kohlschutter and Ehlers, *Z. Electrochemie*, 1912, 18, 373.

The factor 1.25 is the heterogeneity factor and has this value for the particular size range mentioned above. Since r is the average value of the radius it will obviously depend upon the age of the smoke and may be calculated as follows.

If the size range is 1 to 7

$$\text{then } \frac{n}{7} \cdot \frac{4}{3} \pi \rho (x^3 + (2x)^3 + \dots + (7x)^3) = M \times 10^{-9}$$

where n is the number of particles per c.c., ρ their density, x the radii of the smallest and M the concentration of the cloud in mgms. per cubic metre.

Therefore the average radius r of the particles will be

$$r = 4x = 4 \sqrt[4]{\frac{M \cdot 10^{-9}}{\frac{4}{3} \pi \rho \cdot 1.25 \cdot n}}$$

It is interesting to note that the average radius calculated in this way is only about 0.81 of that calculated by assuming that all the particles are of equal radii.

The above expression has been applied to our smokes and the dotted lines in Fig. 4 give the theoretical curves so calculated. The only effect of the reduction of the pressure upon the equation is to increase the value of l , the mean free path of the gas.

It will be seen that the theoretical curve calculated for the smokes at atmospheric pressure is in good agreement with the experimental curve. The agreement, however, is not at all good at the lower pressures. This is due to the fact that the rate of coagulation of any two particles of radii r_1 and r_2 is proportional to the factor $\left[\left(1 + \frac{Al}{r_1} \right) + \left(1 + \frac{Al}{r_2} \right) \right]$

The change of this term with pressure is not constant for different values of r_1 and r_2 , consequently the size distribution and heterogeneity of the smokes must alter quite appreciably with change of pressure, even though the mass concentration is kept constant. Thus we should not expect the equation which agrees with results taken at atmospheric pressure to agree with those at reduced pressure unless allowance can be made for the alteration in size distribution.

It must be borne in mind when considering these ferric oxide aerosols that on account of the chain-like character of the aggregates in the later stages of coagulation, the particles even in the earlier stages may deviate considerably from the spherical in form, and the applicability of the Smoluchowski theory modified in the above manner to these may well be questioned. We are led, therefore, to the conclusion that though this theory provides a useful qualitative hypothesis for the explanation of the kinetics of the coagulation of aerosols in general, it cannot be expected to express quantitatively the coagulations of more complex systems such as these ferric oxide smokes, although for certain systems, such as stearic acid, the correspondence between experiment and theory is very close.

Summary.

A study has been made of the coagulation of ferric oxide aerosols dispersed by the photochemical decomposition of iron carbonyl in presence of air at pressures of 760, 400, and 200 mm. The particulate volume

graphs are found to be linear but their slope becomes steeper as the pressure falls.

The values of σ_0 differ markedly in the three cases and indicate that the smokes formed at lower pressures start from larger primary particles.

Microscopic examination of the aggregates confirms this conclusion. The limitations of Smoluchowski's theory when applied to smokes of this type are discussed.

GENERAL DISCUSSION.

Mr. C. H. Bosanquet (*Billingham*) said: The fact that the straight lines showing $1/n$ in terms of t at different pressures do not cut the axis of zero time at the same point may be due to the l/r term in Smoluchowski's equation being predominant in the initial stages when r is very small. This would cause pronounced curvature of the lines near the origin, the effect being more marked at the lower pressures. Comparison of the values of n after equal lapses of time would not then give directly comparable results, accounting at least in part, for different mean particle sizes being found.

Dr. W. Cawood (*Leeds*) said in reply: If the theoretical curves shown by the dotted lines in Fig. 4 are calculated by assuming $\sigma_0 = 0$, then the l/r correction will not give the required curvature. In practice the curves for the low pressure results, calculated with this assumption are more or less parallel to those given in Fig. 4, but start from zero. The only way to obtain an even approximate agreement between theory and experiment seems to be to assume the initial number obtained by a linear extrapolation of the experimental results.

The effect of the l/r correction may be shown approximately by solving the equation given in the paper for σ_0 .

$$\text{Thus} \quad \sigma_0 = t \cdot \frac{4}{3} \frac{RT}{\eta N} \left(1 + \frac{Al}{r} \right) - \sigma$$

using the experimental values for σ and t . Since at the low pressures the experimental points do not lie exactly along the theoretical curve, the values for σ_0 will not be the same for the different experimental values of σ and t , but the values of σ_0 so obtained are not widely different from those obtained by a linear extrapolation.

The empirical correction for radius in Harper's theory certainly tends to make the curvature smaller, but this correction, which incidentally appears to be given more rigidly by Fuch's treatment of Smoluchowski's equation only applies to particles smaller than about 3.5×10^{-8} cms. radius. In our clouds the particles are larger than this after two or three minutes and consequently the extrapolation would not be greatly changed.

Dr. W. R. Harper (*Bristol*) said: The extrapolation of the particulate volume/time graph as a straight line to zero time is inconsistent with the variation of the coagulation coefficient for small particle size implied by the formula assumed in the paper, and though the variation is less on my own theory, it would still be sufficient to invalidate any conclusions concerning the existence of primary particles drawn from this extrapolation.

Mr. A. G. Grant (*Darlington*) said: In the formation of a particle of, say, 10^4 molecules from a condensing vapour, there must first be a union of two or more molecules, this first group growing until it reached the size of Whytlaw Gray's "primary particle." Although considerations of coagulation apply to these "primary particles," further extrapolation of the curves showing particles size against time, should lead to a bi-molecular particle, unless there is some discontinuity. In other words, either the "primary particle" is a somewhat arbitrary unit, or it represents a point of discontinuity.

Dr. R. Lessing (*London*) suggested that the differences observed at varying pressure may be due to the chemical mechanism of the decomposition of iron carbonyl rather than to the behaviour of its vapour. In

the commercial production of nickel from its carbonyl slight variations in the temperature of decomposition changed the structure of the fresh metal bloom deposited on the old nickel pellets. Dewar¹ has shown the influence of pressure on the temperature of decomposition of nickel carbonyl.

Mr. C. F. Goodeve (*London*) said: What is the exact meaning of the term "primary particle," as used in this paper and the introductory paper. The term seems to imply some clearly defined intermediate state between the original molecular dispersion and the colloidal one obeying a bi-molecular coagulation law. The extrapolation to zero time does not seem to be very useful, because it depends on a too accurate measurement of time and definition of the starting-point.

It is necessary also to consider the mechanism of the formation of ferric oxide smokes. The question as to the necessity for condensation nuclei before the formation of smokes or fogs has often been discussed. I am attempting to build up a quantitative theory based on initial clustering of the molecules in a supersaturated gas—a theory somewhat on the lines suggested by Volmer.² It is now possible to determine approximately the heat of formation of clusters of 2, 3, 4, etc., molecules, knowing only the latent heat of evaporation of one molecule from a flat surface of the solid or liquid substance. As a rough approximation, the energy required to separate two molecules in contact in a cluster, is one-tenth of that required to remove one molecule from a flat surface. The energy required to remove one molecule from a triple cluster is about twice this and, from a quadruple cluster, less than three times. The latent heat of evaporation of ferric oxide from a crystal is probably not known, but would be greater than 100,000 Cals. per gram molecule. This means that, if two ferric oxide molecules collide and are relieved of their excess energy by radiation or by collision with gas molecules, they would require about 10,000 Cals. per gram molecule energy to break them apart. This amount of energy could rarely be obtained at room temperature, where the average energy per degree of freedom would be a few hundred Calories. Double clusters, once formed, would grow very rapidly to larger clusters and eventually to smoke particles. It is seen therefore, that, in the case of ferric oxide, it is entirely unnecessary to have nuclei present before condensation could occur.

These considerations, however, do not apply to super-saturated water vapour. Two-molecule clusters are held together by only about 1000 Cals. and would be very readily broken up on collision with gas molecules.

From these considerations it is very difficult to see how, with ferric oxide, any discontinuity in the condensation process could occur. The building up of clusters and their coagulation to larger particles would be a smooth continuous process, following approximately the considerations given.

Mr. G. W. Slack (*Leeds*) said: The number of *primary particles* is dependent upon the rate of formation of nuclei and upon their rate of growth when formed. The former (in the case of smokes of Fe_2O_3 and similar substances of vanishingly low vapour pressure) is probably equal to the number of molecular collisions and will therefore be independent of the nature of the medium, whilst the latter (being governed by the diffusion of vapour to the surface of these nuclei) is assisted by the increased mobility due to the lower pressure in the case of the experiments at 200 mm. and 400 mm. The combined result is that fewer nuclei have time to be formed in the short interval before supersaturation is relieved.

Professor Dr. G. Jander and Dr. K. E. Stump (*Greifswald*) (*communicated*): This work emphasises the great importance of such photochemical reactions in the investigation of those aerosols in which the readily volatile material forms a substance of very low vapour pressure and a gaseous product, e.g. by the interaction of the oxygen of the air in

¹ *J. Chem. Soc.*, 1904, 86, II., 488.

² M. Volmer, *Electrochem.*, 1929, 35, 555.

the photolysis of iron pentacarbonyl vapour to produce iron oxide, dust and carbon oxides.

The authors' results agree with those of our own recent work, qualitatively but not quite quantitatively, therefore fuller quantitative investigation of this whole complex question is needed; we shall therefore repeat the more fundamental measurements with every precaution to avoid experimental error.

Dr. N. Fuchs (*Moscow*) (*communicated*): The chief difficulty in the investigation of the formation of aerosols lies in strictly separating the two quite different processes involved, *viz.*, the condensation of vapours and the coagulation of the primary aerosol. This may be done either by "fixation" of the primary aerosol by very strong dilution or, as done by Cawood and Whytlaw-Gray, by extrapolation of the numbers of particles per c.c. found in a coagulating aerosol to the moment of its formation. The second important obstacle (the difficulty of obtaining uniform supersaturation throughout the whole volume of the vapour) is completely removed in the photochemical method of smoke formation used in this work. We could therefore say that the experiments of Cawood and Whytlaw-Gray were made under ideal conditions except for the relatively long (6 min.) time spent in the formation of the smoke.

The chief result of these experiments (the increasing of the dispersity of the primary smoke with the air-pressure) can be interpreted unequivocally from the view-point of the modern theory of nuclei formation in supersaturated systems.³ Since, according to this theory, the number of nuclei formed in unit of time must be independent of the air-pressure, the result mentioned can only be caused by different rate of growth of the nuclei. For particles considerably smaller than the mean free path of the gas-molecules, the rate of growth is also independent of the air-pressure: ⁴ a perceptible difference in the rate of growth at different pressures will begin only when the growing particles have reached the size of about 10^{-4} to 10^{-5} cm. Henceforth they will grow the faster, the larger the coefficient of diffusion of $\text{Fe}(\text{CO})_5$ vapour, *i.e.* the less the air-pressure.

Dr. W. Cawood (*Leeds*) said: With reference to Mr. Goodeve's suggestions as to the formation of condensation nuclei from the molecules of ferric oxide itself, I am in complete agreement. Indeed, we meant to imply such nuclei in the paper.

The difference between condensation from supersaturated vapour and coagulation, I consider to be quite sharp and defined. In condensation, the molecules of the supersaturated vapour collide and an amount of energy equivalent to the energy of formation of the solid is dissipated, a homogeneous primary crystal or particle being thus formed after a sufficient number of molecules have condensed. In coagulation, however, we have the case of two of these primary crystals colliding. They do not in general form one crystal (except in the rare case of the correct edges coinciding and even then an adsorbed layer of gas might keep them separated) nor do they dissipate energy because they are already in the solid phase. This type of coagulation would form the loose-chain-like aggregates which we observed.

Thus, we see that whilst condensation builds up homogeneous particles or crystals, coagulation (in the case of solids) forms aggregates. Moreover, the first process, with a substance like ferric oxide would be much faster than the second. It appears very likely therefore, that in the formation of such smokes, primary crystals are really formed initially and almost instantaneously by condensation, whilst coagulation is a secondary process.

Professor R. Whytlaw-Gray (*Leeds*), in reply, said: Little is known about the initial stages in the formation of smoke. As Mr. Goodeve has pointed out, in systems of non-volatile particles such as those of ferric

³ Becker and Döring, *Ann. Physik.*, 1935, **24**, 719.

⁴ Fuchs, *Physik. Z.d. Sowjetunion*, 1933, **4**, 481.

oxide it is very unlikely that any of the small molecular clusters first formed split up again, as is the case with volatile systems, and it might be contended that the process is a continuous one of progressive aggregation from the molecular to the particular state. If this were so, a freshly formed smoke should always be heterogeneous and contain all sizes of particles and this heterogeneity should persist during coagulation, giving an extended size distribution of the Smoluchowski type. On this view I agree that the term "primary particle" would be difficult to define. It appears to me, however, that the process is not a continuous one. As a result of molecular encounters a certain number of larger clusters will be formed which contain sufficient molecules to give crystalline units or super-cooled droplets. These will then act as nuclei or centres of condensation for the molecules and smaller clusters, and the system formed finally will be approximately homogeneous.

This apparently is what happens in the formation of a gold sol; primary particles of crystalline gold are formed and, as Zsigmondy and others have shown, the process is dependent on the rate of formation of nuclei and the rate of crystallisation.

If this interpretation can be applied to a smoke, compact particles, often crystalline, will first be formed, these are the primary particles. These will immediately begin to coagulate, and will form later the complexes of loose or chain-like structure which we see in the microscope. The units composing these complexes can, in the case of many smokes, be separated by peptisation with suitable solutions to form hydrosols (as Kohlschütter has shown) but the size of the particles in these has not been determined.

Coagulation, then, is the linking together of compact solid units, which may be crystalline or amorphous, and seems to me to be essentially different from the processes of molecular condensation by which the smoke is formed. Probably the two processes go on simultaneously to some extent and in the early stages the multiple particles formed by coagulation may be cemented together by condensation.

THE MOVEMENT OF DUST OR SMOKE PARTICLES IN A TEMPERATURE GRADIENT.

By W. CAWOOD.

Received 31st March, 1936.

The existence of a dark space round a hot body in a smoke or dust was first observed and studied by Aitken. Since then the size of the dark space and its relations with temperature difference and pressure have been studied by various observers, but no quantitative explanation of the phenomena has been put forward. The effect is almost certainly not due to the radiant energy of the body, for the particles of dust or smoke are in continuous rotation and consequently have an even surface temperature. Also there appears to be no reason why the dark space should have a sharp edge if the phenomenon be due to radiation. Finally, quite a strong effect may be observed at the edge of a solid body only about 10° C. higher than the surrounding air, when the radiation would be extremely small, and moreover the dark space does not appear to be dependent upon the nature of the solid surface.

A consideration of the mechanism of the conduction of heat from solid bodies to gases appears to afford a clue to the true explanation of the effect.

It is well known that when a solid body is heated by a flame, there is a sharp temperature gradient near to the surface of the solid.* Thus, an old experiment is to boil a kettle with a piece of paper stuck on the bottom. The paper does not char, showing that the hot gas molecules do not actually reach it. The dark space may be observed if the velocity of the flame is not too great, and may reach a thickness of about 2 to 3 mm. If the upward velocity of the flame is increased the dark space gets thinner, but never entirely disappears. This one would expect, because the temperature gradient near to the cold surface is set up at a velocity of the same order as the molecular velocities, whilst the blast velocity of burning gas is much smaller.

It is interesting to note, however, that if a smoky flame is used, although the dark space may be observed with ease, the solid particles of carbon are projected through it and deposited on the cold surface, the reverse effect of the dark space round a hot body in a smoke.

This affords a clue to the latter phenomena, *i.e.*, that there is a force which tends to move small particles down a temperature gradient. In other words, that smoke particles will tend to be repelled by a hot body and be attracted by a colder one.

Let us now consider the conduction of heat between solids and gases in greater detail. Consider an infinite flat plate at a temperature T_1 and a gas below it at a lower temperature T_2 , and from the foregoing let us assume that the total temperature gradient is contained in a small strip of gas near to the hot plate. If now there were no convection currents, that is, mass movements of the gas, then if we take any small surface in the temperature gradient

$$N_1 c_1 = N_2 c_2$$

where $N_1 N_2$ are the number of molecules per cubic centimetre on each side of the surface with components perpendicular to the surface, and c_1, c_2 are their average velocities corresponding to the difference of temperature dT . This of course is the relationship which Knudsen¹ finds to hold at low pressures and through small apertures.

Consequently

$$\frac{N_1 c_1^2}{N_2 c_2^2} = \frac{c_1}{c_2}$$

$$\therefore \frac{p_1}{p_2} = \sqrt{\frac{T_1}{T_2}}$$

and

$$\frac{N_1}{N_2} = \sqrt{\frac{T_2}{T_1}}$$

If, then, there were no convection, the pressure of the gas near the hot plate would be higher than at distances more remote. In practice, no pressure differences are to be detected under a horizontal hot plate even with an accurate oil gauge. This is because convection is present and the above assumptions do not hold good. As Knudsen¹ has shown, the pressure difference can be observed and indeed confirms the square root law, only if convection is obviated by connecting the two vessels containing gases at a different temperature by means of tubes of radius of the same order as the mean free path of the gas.

* This is known as the skin effect in engineering. Measurements of the heat conductivity from gases to solids appear to give the gradient as about one-tenth of a millimeter wide.

¹ M. Knudsen, *Ann. Physik*, 1909, 28, 75, 999; 1910, 32, 809.

It must be emphasised, however, that although convection destroys the pressure differences it does not destroy the temperature gradient. As is shown by the flame experiments, the gradient may be made steeper by the quick mass movements of the gas, but is never entirely destroyed.

Let us now consider a small cylinder of gas in the temperature gradient, of length about twice the mean free path of the gas. If the cylinder has a sufficiently small radius, convection currents will not affect the movements of the molecules parallel to the axis of the cylinder, for the perpendicular velocity gradient of a convection current is not continuous, but must vary in steps of the order of magnitude of the mean free path of the gas. Consequently the velocity on both sides of such a cylinder will be approximately equal. Such a cylinder will therefore move bodily in the current, but the temperature difference between the ends will be the same, and apart from the average temperature being altered, the cylinder will otherwise be unaffected. Consequently in this very small cylinder one would expect Knudsen's laws to be obeyed.

Consider now a smoke or dust particle in the middle of the cylinder. It will be bombarded by gas molecules moving in all directions but it is only necessary to consider the bombardments due to molecules moving perpendicularly to the plate, and if F is the force per unit area parallel to the plate then the total force on the one side of a spherical particle is

$$\int_0^{\pi/2} F \cdot 2\pi r^2 \sin \theta \cdot \cos \theta \cdot d\theta \\ = F \cdot \pi r^2.$$

The force on the spherical particle due to the bombardment of the gas molecules may now be calculated in a similar manner to that in which Einstein² calculated the force on a vane radiometer.

Thus $\frac{1}{2}N_1c_1(\pi r^2)$ molecules will collide with the particle on one side and $\frac{1}{2}N_2c_2(\pi r^2)$ on the other, where N and c have their usual significance. The difference of velocities of the molecules accounts for the heat flow.

Thus the heat flow if the particle was not there

$$= (\pi r^2)f = \frac{1}{2}N_1c_1 \cdot (\pi r^2) \cdot \frac{mc_1^2}{2} - \frac{1}{2}N_2c_2(\pi r^2) \cdot \frac{mc_2^2}{2} \\ = \frac{1}{2}N_1c_1(\pi r^2) \left[\frac{mc_1^2}{2} - \frac{mc_2^2}{2} \right] \quad . \quad . \quad . \quad . \quad (1)$$

where f = heat or energy flow per unit area ;

m = mass of gas molecules.

If c_1 and c_2 are the velocities appropriate to the temperatures at the place of the last collision, *i.e.*, at the ends of the cylinder then

$$\frac{1}{2}mc^2 = \frac{3}{2}RT$$

$$\text{and} \quad \frac{1}{2}m(c_1^2 - c_2^2) = - \frac{3}{2}R \cdot \frac{dT}{dx} \cdot 2L$$

where L = mean free path of gas.

$$\therefore f = - \frac{1}{2}N_1c_1 \cdot R \cdot \frac{dT}{dx} \cdot L \quad . \quad . \quad . \quad . \quad (2)$$

² A. Einstein, *Z. Physik*, 1924, **27**, 1.

If now we consider the smoke particle then there will be excess of momentum (k) away from hot plate

$$\begin{aligned} \text{i.e.,} \quad k &= \frac{1}{2}N_1c_1(\pi r^2) \cdot mc_1 - \frac{1}{2}N_2c_2(\pi r^2) \cdot mc_2 \\ &= \frac{1}{2}N_1c_1(\pi r^2)[mc_1 - mc_2] \end{aligned} \quad (3)$$

and if the impulse due to recoil is neglected then k = force on particle

$$\begin{aligned} \therefore k &= \frac{\pi r^2 f}{c} \text{ (from (1) and (3))} \\ &= -\frac{1}{2}N_1R \cdot \frac{dT}{dx} \cdot L \cdot \pi r^2 \text{ (if } c = \frac{c_1 + c_2}{2} \text{ and } c \text{ is very nearly } = c_1) \\ &= -\frac{1}{2}p \cdot \frac{dT}{dx} \cdot \frac{L}{T} \cdot \pi r^2 \end{aligned} \quad (4)$$

If a smoke particle moves under a constant disturbing force k , however, we have

$$k = \frac{6\pi\mu rV}{\left(1 + \frac{AL}{r}\right)}$$

V = velocity ; μ = viscosity of gas ; A = constant.

As the edge of the dark space acts as a semi-permeable membrane the smoke as a whole exerts an osmotic pressure on the edge of the

equal to $\frac{RT}{N} \cdot n$ where n = number of particles per 22.2 litres.

For a particle this is the component of the Brownian motion on the

and is therefore $\frac{RT}{N}$ and the force of one particle on the space is

r^2 . Consequently

$$\begin{aligned} \frac{1}{2} \cdot p \cdot \frac{dT}{dx} \cdot \frac{L}{T} \cdot \pi r^2 &= \frac{6\pi\mu rV}{\left(1 + \frac{AL}{r}\right)} + \frac{RT}{N} \cdot \pi r^2 \\ \therefore V &= \frac{\left(\frac{1}{2} \cdot p \cdot \frac{dT}{dx} \cdot \frac{L}{T} \cdot \pi r^2 - \frac{RT}{N} \cdot \pi r^2\right)}{6\pi\mu r} \cdot \left(1 + \frac{AL}{r}\right). \end{aligned}$$

The velocity given by the above equation is the velocity in the small cylinder of gas which we have considered. If, as actually happens, there is a convection current towards the plate, the actual velocity will be reduced, because the cylinder will be moving bodily in the current and if the convection is fast enough the dark space should not be observed at all. As will be seen later this is confirmed by experiment. Also, although the velocity appears to be proportional to the radius of the particle this is not actually the case, for the fundamental assumption is that the radius should be of the same order as the mean free path of the gas (i.e. about 10^{-5} cms.). If the radius is much larger than this, then if the dust-free space is due to molecular bombardment, the force will be destroyed by the convection effects and very large particles ought not to move away from the hot body. According to other observers this actually is the case.³

³ H. H. Watson, *this discussion*.

If the temperature gradient is linear over the region of the dark space, then the time taken for a particle to move from the plate to the edge of the dark space may be calculated as follows.

From the last equation (neglecting the $\frac{RT}{N} \cdot \pi r^2$ term)

$$V = \frac{dx}{dt} = \frac{K}{T}$$

where

$$K = \frac{\frac{1}{2}p \cdot \frac{dT}{dx} \cdot L \cdot r}{6\mu} \cdot \left(1 + \frac{AL}{r}\right)$$

and if $\frac{dT}{dx}$ is constant

$$\text{then} \quad T_x = \frac{dT}{dx} \cdot x + T_G$$

where T_G is temperature of gas.

$$\begin{aligned} \therefore \frac{dx}{dt} &= \frac{K}{\left(\frac{dT}{dx}\right) \cdot x + T_G} \\ \therefore t &= \left(\left(\frac{dT}{dx}\right) \cdot \frac{x^2}{2} + T_G \cdot x \right) \cdot \frac{1}{K} \\ &= \frac{\left(\frac{dT}{dx}\right) \cdot \frac{x^2}{2} + T_G \cdot x}{\frac{1}{2}p \cdot \left(\frac{dT}{dx}\right) \cdot L \cdot r \left(1 + \frac{AL}{r}\right)} \cdot 6\mu \quad (5) \end{aligned}$$

Some rough experiments have been carried out in order to see if the last equation gives values of the right order. A small ultramicroscope cell was constructed in which the top of the cell was a flat brass plate, which was also the bottom of a hollow chamber through which steam could be passed. The cell was illuminated by an arc beam, which was focused so that the edge of the beam was just touching the brass plate. Into this cell was blown tobacco smoke. The dark space was immediately observed, and with steam going through the plate, the thickness was about 0.08 cms. in the middle. Towards the edge the thickness was rather smaller, due presumably to the slightly lower temperature of the edges of the plate, which were in contact with the ebonite cell. Underneath the dark space there was a general convection current, upwards towards the hot plate, but the particles rising in the current did not penetrate into the dark space. The whole appearance was as though there was an invisible barrier, through which the gas rose but not the particles. By blowing into the cell, the dark space was momentarily destroyed, and then all the particles began to move away from the plate with a roughly uniform velocity. The time taken for the particles to move from the edge of the plate to the edge of the dark space was about 3 seconds. As the convection current upwards was of about the same order the true velocity through the gas was about twice that actually measured. Consequently the time taken to move through the dark space was about 1.5 secs.

Let us now see how this agrees with the foregoing calculations. From equation (5)

$$t = \frac{\left(\frac{dT}{dx}\right) \cdot \frac{x^2}{2} + T_G \cdot x}{pL \left(\frac{dT}{dx}\right) r \left(1 + \frac{AL}{r}\right)} \cdot 12\mu.$$

The cell was warmed by contact with the hot plate and thus the temperature of the gas T_0 was on the average about 50°C . and $\frac{dT}{dx} = \frac{50}{0.08} = 625$. The average temperature in the dark space being about 75°C ., the viscosity μ may be taken as 2.1×10^{-4} dynes/cm.² The particles were of about 10^{-6} cms. radius.

Consequently

$$t = 0.59 \text{ secs.}$$

We thus see, that whilst the equation gives a value of the right order, the velocity is actually about three times too great. This is probably because the value taken for $\frac{dT}{dx}$ is too large owing to the temperature gradient not being linear. On the whole, considering the roughness of the experiments, the agreement is satisfactory.

Whilst the above gives the explanation of why the particles move away from a hot body, it does not enable one to calculate the width of the dark space. This appears to be almost impossible because it obviously depends so much upon the convection currents, and consequently the design of the apparatus. It appears as though the temperature gradient is set up at regions very near to a hot body at a speed of the same order as molecular velocities, but that this speed, farther away from the body is much slower, being only of the same order as the ordinary convection effects and the gradient is consequently affected by them.

THE DUST-FREE SPACE SURROUNDING HOT BODIES.

BY H. H. WATSON.

Received 9th March, 1936

1. Summary.

If a hot body is placed in a chamber containing dust or smoke, and if it be illuminated suitably, a well-defined dust-free space is seen surrounding the body and extending above it as a sort of wedge. The particles in the chamber follow the convection currents set up by the hot body, but do not cross the apparent barrier of the dust-free space. The thickness of this space was found to increase as the 0.52 power of the temperature difference between hot body and ambient air, and inversely as the 0.61 power of the air pressure. The magnitude of the space is independent of the nature of the dust or of the particle size; it depends, however, on the size and shape of the hot body, being wider the larger the body, and increasing at twice the rate for vertical plane surfaces that it does for horizontal circular rods. At atmospheric pressure the thickness of the dust-free space A is connected with θ , the temperature excess of the hot body over the ambient air, and H , the convective heat loss per unit area of the hot body per sec., by the following equation:

$$A = L\theta H^{-0.36}$$

where L is a constant, independent of the size of the body, but double the value for vertical plates that it is for horizontal rods.

A review of the various suggestions as to the cause of the dust-free space has been made. There is evidence that it is caused by a differential molecular bombardment on the particles in the very steep and varying temperature gradient near the hot body.

One practical significance of the dust-free space is discussed in a brief reference to the design of the thermal precipitator dust sampling apparatus.

2. Description of Phenomenon.

When a hot body is placed in a chamber containing dust or smoke, and illuminated suitably, it is seen that there is a well-defined dust-free layer embracing the body, and extending above it as a sort of wedge (Figs. 1 and 2). The dust or smoke particles in the chamber follow the convection currents set up by the hot body, but do not cross the apparently impenetrable barrier of the dust-free space.

Tyndall¹ and Rayleigh² observed only the wedge of dust-free air above the body, and Aitken³ and Lodge and Clark,⁴ working almost concurrently, were the first to observe and describe that part of the dust-free space which embraces the body.

Aitken was able to show that the effect is not due to gravitational forces, centrifugal forces, vaporisation of the particles, radiation, or electrical forces, and concluded that it is caused by the stronger molecular bombardment on the particles in a direction away from the hot body.

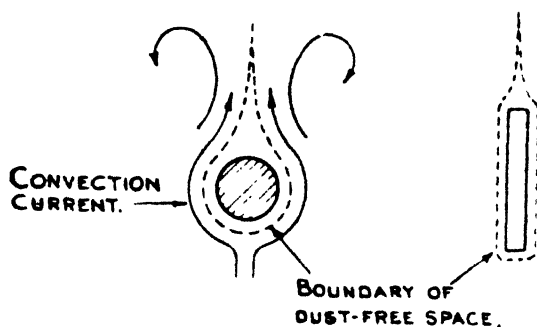


FIG. 1.

Lodge and Clark made a few measurements and concluded that the space increases with increasing temperature of the body, and with decreasing air pressure, and decreases with increasing molecular weight of the gas in which the phenomenon is studied.

The present investigation shows that the thickness of the dust-free space increases with increasing temperature difference between the body and ambient air (equivalent to the walls of the enclosing chamber), at a rate which is rapid at first, but begins to fall off, until at about 70° C. temperature difference it becomes sensibly constant, up to at least 250° C. difference, beyond which measurements were not made (see Fig. 5). The magnitude of the effect depends on the size and shape of the hot body, but not on the nature of that body. Horizontal circular rods and vertical plane surfaces were used in these experiments.

Although the particulate clouds used (principally magnesium oxide) were heterogeneous, with at least a 20 to 1 size range (0.1 μ to 2.0 μ diameter), the edge of the dust-free space is sharp and well defined, indicating that, up to at least 2.0 μ , particles of all sizes are influenced to the same degree. Similarly, the nature of the particulate cloud does not affect the thickness of the space; such widely different substances as magnesium oxide, flint dust, carbon black, tobacco smoke and sulphur "smoke" were used.

¹ Tyndall, J., *Proc. Roy. Inst.*, 1870, 6, 3.

² Rayleigh, Lord, *Proc. Roy. Soc.*, 1882, 34, 414.

³ Aitken, J., *Trans. R. S. E.*, 1884, 32, 239.

⁴ Lodge, O. J. and Clark, J. W., *Phil. Mag.*, 1884, 17, 214.

The space has the same thickness round more than half of a horizontal rod and opposite most of the surface of a vertical plate, in fact, opposite all parts of a hot body not affected by the convection wedge.

There are two complications which may occur in the study of this phenomenon, both of which were observed and accounted for by Aitken. First, the apparent dust-free space may be enlarged considerably, because of the vaporisation of particles with a low boiling-point. Lenher and Taylor⁵ observed this effect, caused by the evaporation of sulphuric acid mist near a hot platinum wire. The cloud produced by burning sulphur in the chamber will give two spaces for high temperatures of the body, the inner one, which is the true dust-free space, quite free from particulate matter, the outer one containing ordinary smoke, but no product of low boiling-point (*e.g.* sulphur tri-oxide) (Fig. 2). Secondly, if moisture or some other liquid is constantly evaporating from the hot surface, an enlarged space is obtained. In this respect it is interesting to note the effect when carbon tetrachloride is evaporating from a rod, which is initially at the same temperature as the surrounding air. A well-marked dust-free space is produced, but the wedge is pointing downwards, as the rod is cooled by the rapid evaporation. This observation supports the theory that the effect is due to a molecular bombardment. No dust-free space is produced merely by cooling the body.

3. Description of Apparatus.

The dust chamber, in which the experiments were made, consisted of a water-jacketed brass cylinder, A, 7.6 cm. long and 8.6 cm. internal diameter (Figs. 3 and 4), clamped firmly with its axis horizontal. The front end was closed by a glass window, B, while a wooden bung, D, with a central brass bush, C, was fitted into the other end.

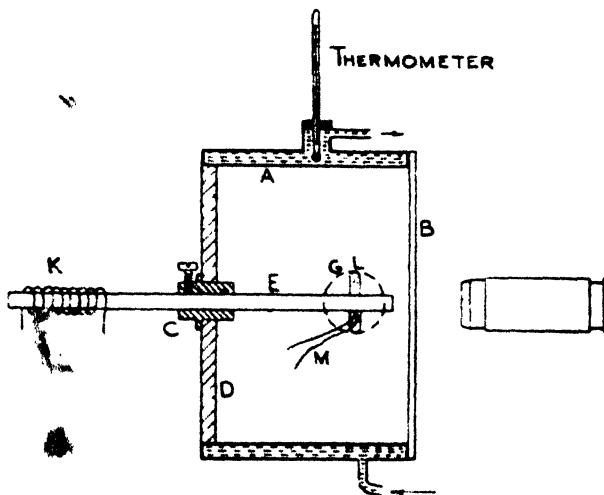


FIG. 3

Five different bodies were used :

- Body A. Vertical plane copper surface, 6.0 cm. high, 3.0 cm. wide.
- Body B. Vertical plane copper surface, 3.1 cm. high, 3.0 cm. wide.
- Body C. Horizontal circular copper rod, 0.90 cm. diameter.
- Body D. Horizontal circular copper rod, 0.46 cm. diameter.
- Body E. Horizontal nichrome wire, 0.0254 cm. diameter.

The rods passed through the bush, and were held in position along the axis of the chamber by a clamping screw. The wire was also supported along the axis, the ends passing out of the chamber through two holes in the bung. The plane surfaces were supported vertically, in the centre of the chamber and along its axis, by a bracket fixed to the bush.

⁵ Lenher, S., and Taylor, G. B., *J. Amer. Chem. Soc.*, 1929, **51**, 2741.

The rods were heated electrically by a resistance coil, K, wound round the end of the rod projecting from the chamber, the heat being conducted along the rod. The wire (Body E), was heated by an accumulator, while the two vertical planes each were made up from two similar plates with a heating coil sandwiched between them.

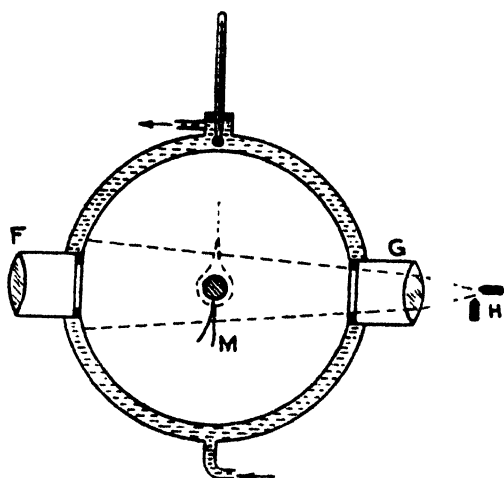


FIG. 4.

A small copper-constantan thermo-couple, M, was used to measure the temperatures of the rods and plates; those of the wire were computed from its electrical resistance.

At a distance of 2.5 cm. from the front of the chamber were two windows, F, G. These were arranged at opposite ends of a horizontal diameter of the chamber, and the light from Zeiss 10 amp. automatic arcs, H, illuminated the hot body through the windows. The windows were covered by a stop, L, so that a ribbon of light, rendered only slightly divergent by a lens, entered the chamber.

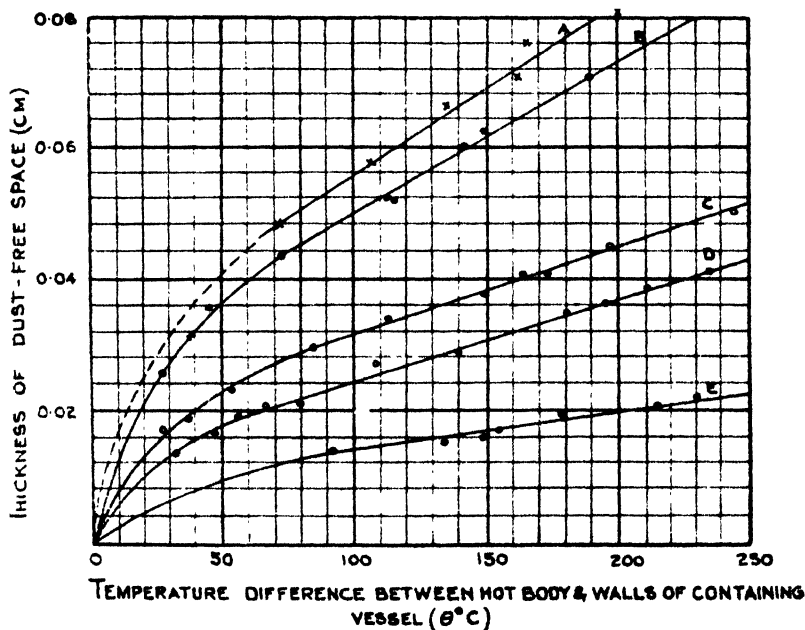


FIG. 5.

A horizontally moving travelling microscope, with its axis parallel to and on the same level as that of the chamber was used to observe and measure the dust-free space. Visibility of the space was better and measurements easier to make when dense clouds were used. Multiple scattering of light inside the chamber was reduced to a minimum by painting the walls a dull black.

The water jacket, through which tap water was running, kept the walls of the chamber at a constant measured temperature.

The thickness of the dust-free space was measured for the five bodies for temperature differences up to about $250^{\circ}\text{C}.$; all measurements were made horizontally outwards from the surface of the body.

4. Results.

Measurements of the thickness of the dust-free space were made, using magnesium oxide smoke, produced by burning magnesium ribbon (Table I.).

5. Accuracy of Measurements.

The thickness of the dust-free space was measured to within 0.0005 cm. The focusing of the microscope was somewhat coarse due to the large depth of focus of the optical system, and errors of about ± 3 per cent. were possible. This error would be the same for the whole of one set of observations, during which the microscope was usually not re-focused. Temperatures were measured to the nearest degree Centigrade.

6. Interpretation of Results and Empirical Formulæ.

The results show that the dust-free space increases in thickness with increasing temperature difference between the hot body and the ambient air. For any one temperature it also increases with the linear dimensions of the hot body (diameter of a horizontal rod, and height of a vertical plate).

Figures for smokes and dusts other than magnesium oxide have not been reproduced, but within the experimental error of about ± 3 per

TABLE I.*

Temp. of Water Jacket. ($^{\circ}\text{C}.$)	Temp. of Hot Body. ($^{\circ}\text{C}.$)	Temp. Difference. θ ($^{\circ}\text{C}.$)	Thickness of Dust-Free Space. A (cm.).
Body A. Vertical plane surface, 6.0 cm. high, 3.0 cm. wide.			
17	56	39	0.032
	88	71	0.048
	124	107	0.058
	154	137	0.066
	181	164	0.071
	184	167	0.076
	218	201	0.081
	248	231	0.092
	286	269	0.097
Body B. Vertical plane surface, 3.1 cm. high, 3.0 cm. wide.			
16	44	28	0.0275
	61	45	0.0355
	88	72	0.043
	128	112	0.052
	131	115	0.052
	158	142	0.060
	165	149	0.062
	206	190	0.0705
	261	245	0.083
Body C. Horizontal circular rod, 0.90 cm. diameter.			
10	37	27	0.017
	48	38	0.0195
	64	54	0.023
	96	86	0.0295
	122	112	0.034
	159	149	0.038
	174	164	0.0405
	182	172	0.041
	206	196	0.0445
	254	244	0.0495
Body D. Horizontal circular rod, 0.40 cm. diameter.			
10	42	32	0.0135
	57	47	0.0165
	66	56	0.019
	76	66	0.0205
	90	80	0.0215
	118	108	0.027
	150	140	0.029
	190	180	0.0345
	205	195	0.036
	221	211	0.0385
	245	235	0.041
Body E. Horizontal wire, 0.0254 cm. diameter.			
10	92	82	0.0135
	143	133	0.015
	158	148	0.016
	164	154	0.017
	187	177	0.0195
	223	213	0.0205
	240	230	0.022

* These results are plotted in Fig. 5.

cent. they agree with those for magnesium oxide. The figures of Table I. were plotted on logarithmic scales and the following general relation between A and θ obtained:—

$$A = K\theta^\alpha \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where A is the thickness of the dust-free space, θ is the temperature difference, K and α are constants.

The values of K and α for the different bodies are given in Table II.

Miyake⁶ has made recently some measurements of the dust-free space surrounding vertical platinum ribbons, 3 to 10 cm. long and 0.5 cm. wide. He found that the thickness of the space increased as the 0.7 power of the temperature difference.

To obtain a single formula for all bodies, the way in which K varied with the shape and size of the body was studied. The rate of convective heat loss from a hot body is given by:—

$$H = C\theta^{1.25} \quad . \quad . \quad . \quad (2)$$

Mean value of $\alpha = 0.52$

where H is the convective heat loss per sec. from unit area of the hot surface, and C is a constant which

varies with the shape, size and orientation of the body. The value of C has been determined experimentally for horizontal rods and vertical planes. It is independent of the length of rod and width of vertical plane, and its values for the five bodies have been obtained from curves given by Fishenden and Saunders,⁷ and are tabulated in Table III., θ being given in °C. and H in calories per sq. cm. per sec.

TABLE III.

Body.	Value of C of Equation (2).
A	1.03×10^{-4}
B	1.53×10^{-4}
C	0.93×10^{-4}
D	1.25×10^{-4}
E	5.87×10^{-4}

TABLE IV.

Body.	Value of L .
A	15.2×10^{-5}
B	15.9×10^{-5}
C	8.2×10^{-5}
D	7.1×10^{-5}
E	7.4×10^{-5}

The best relationship between C and K is:—

$$K = LC^{-0.38} \quad . \quad . \quad . \quad . \quad (3)$$

where L is a constant.

The equations now reduce to:—

$$A = L\theta H^{-0.38} \quad . \quad . \quad . \quad . \quad (4)$$

Values of L , obtained by substituting the actual recorded values of A and θ , and the calculated values of H in equation (4) are given in Table IV.

⁶ Miyake, S., *Report of the Aeronautical Research Institute, Tokyo University*, 1935, 10, 85.

⁷ Fishenden, M., and Saunders, O. A., *Calculations of Heat Transmission*, p. 103 (London, H.M.S.O., 1932).

The mean value of L for vertical planes is thus 15.6×10^{-5} , and for horizontal rods 7.6×10^{-5} . It is interesting to note that L is almost double the value for vertical planes that it is for horizontal rods. We may obtain, therefore, the thickness of the dust-free space for horizontal rods and vertical planes of any size from equations (5) and (6).

Horizontal rods :—

$$A = 7.6 \times 10^{-5} \theta H^{-0.38} \quad . \quad . \quad . \quad (5)$$

Vertical plane surfaces :—

$$A = 15.6 \times 10^{-5} \theta H^{-0.38} \quad . \quad . \quad . \quad (6)$$

where A is in cm., θ in degrees Centigrade, and H in calories per sq. cm. per sec.

7. Effect of Air Pressure on the Dust-Free Space.

W. G. Iles has extended this work and has investigated the effect of air pressures less than atmospheric on the thickness of the dust-free space. He used an electrically-heated vertical plane surface 3.1 cm. high (Body B), and made measurements at five different temperatures, determining the thickness of the space at various pressures for each temperature of the body. He found that, at any one temperature, the thickness of the dust-free space opposite the plane vertical surface, 3.1 cm. high, varied inversely as the 0.61 power of the pressure, P . His results are summarised briefly in Table V.

For the plane vertical surface, therefore, we may combine the variation of A with θ and P in the one equation :—

$$A = B^1 \theta^{0.52} P^{-0.61} \quad . \quad . \quad . \quad (7)$$

TABLE V.

Temp. Difference θ (°C.).	Value of C in Formula $A = BP^{-C}$.
41	0.61
68	0.63
88	0.59
145	0.58
181	0.61
Mean value of C : 0.61	

The relation between thickness of dust-free space and air pressure, calculated from the figures given by Lodge and Clark (*loc. cit.*,⁴ p. 226) for a horizontal rod of carbon give :—

$$A \propto P^{-0.65}$$

It appears therefore that the pressure effect and formula (7) is the same for all bodies, although this will have to be verified by further experiments, especially as Miyake,⁶ found for a vertical platinum ribbon that :—

$$A \propto P^{-1.0}$$

8. Review of Suggested Explanations of Phenomenon.

The idea of a simple differential molecular bombardment on the particles to produce the dust-free space does not explain why the edge of the space is fixed and well defined. It can be proved that, due to the differential molecular bombardment in a temperature gradient, there should be a force on a small particle, which is directly proportional to the temperature gradient dT/dx . A temperature gradient exists at every point between the hot body and the walls of the experimental chamber, but the dust-free space does not grow to fill the chamber. There must be some retarding action which stops the effect at a small distance, A , from the hot body. It seems possible that, in the rapidly moving convection stream, the effect of the thermal force does not have time to develop beyond a certain distance.

demand the Magnus effect to produce a drift away from the body. No dust-free space is observed, however, opposite a body which is colder than or at the same temperature as the air streaming past it; it is only formed round a hot body. The Magnus effect, therefore, does not produce a dust-free space.

It seems fairly certain that the phenomenon is produced by a differential molecular bombardment, and for this to be effective the value of dT/dx must be above a certain minimum; this minimum depending on the temperature difference between hot body and ambient air and the rate of convective heat loss.

9. Thermal Precipitator Dust Sampling Apparatus.

Consider a wire, W , (seen in section in Fig. 6) placed in a horizontal position centrally between the two opposite plane surfaces, A and B , of a narrow vertical channel; suppose that the wire is heated to a temperature at which the thickness of the dust-free space in free air is at least as large as the distance between the wire and either plane surface. Then, if air containing dust or smoke is drawn down towards the wire the particles will not be able to penetrate the dust-free barrier extending across the channel. The particles will be deposited just above b and b^1 , where the dust-free space comes into contact with the surfaces. The air, freed from particles, will pass by the wire.

This, briefly, is the principle on which the thermal precipitator dust sampling apparatus¹⁰ has been constructed. A wire similar to body E , 0.0254 cm. diameter, is used and the deposit of dust or smoke is obtained on cover-glasses arranged just within the dust-free space. The dust record can be examined microscopically.

This dust sampling instrument is practically 100 per cent. efficient, a feature which makes it very suitable both in the laboratory and in factories and mines for estimating accurately the dust or smoke concentration.

My thanks are due to Mr. J. D. Fry, who suggested this investigation, for his continued interest and advice.

¹⁰ Green, H. L., and Watson, H. H., *Medical Research Council, Special Report Series*, No. 199 (H.M.S.O., 1935).

GENERAL DISCUSSION.*

Mr. C. H. Bosanquet (*Billingham*) said: At high pressures with large connecting tubes between the bulbs the Knudsen thermal pressure difference effect breaks down, not through convection, but owing to the return flow due to gas pressure. The initial rate of thermal transpiration is proportional to the temperature gradient and the cross-section of the tube. The return flow is proportional to the pressure gradient, and the square of the cross section. Unless the capillary is very small, the full Knudsen pressure difference cannot then be approached.

The number of molecules approaching the hot plate must be equal to the number leaving it in the same time, but their mean velocity is less,

* On two previous papers.

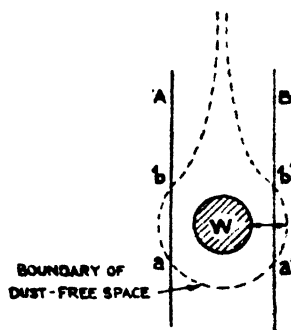


FIG. 6.

giving a transport of momentum away from the plate, and driving away the particles in a manner analogous to the action of a Crookes' radiometer. This should show up as a force on the plate, though a search tube would not necessarily show a pressure, since the temperature gradient at its mouth would be less than that at the surface of the plate.

Dr. T. L. Ibbs (*Birmingham*) said: The work of both authors leads to the conclusion that the dust-free space round a hot body is directly associated with the temperature gradient. This effect is similar to the thermal diffusion effect¹ in gases; simple experiments we have made from time to time on smokes appear to confirm the influence of the temperature gradient on the separating effect.

Chapman² has considered the question of brownian displacements and thermal diffusion of grains suspended in a fluid, and predicted a separating effect. In a smoke suspension there are therefore all the conditions required for a thermal separating effect; and the dust sampling apparatus described by Watson shows the practical efficiency of a temperature gradient as a separating device. Tentative calculations made by Dr. B. E. Atkins support the idea that the separation produced by a small temperature difference might be considerable. The question raised by Sir Robert Robertson as to the cause of the black marks on walls near radiators and steam pipes appears to be explained by the tendency of dust particles to move down a temperature gradient, causing them to be deposited on a cold surface.

The apparatus used in many experiments on this subject has taken the form of a hot wire in a large enclosure, and the dust-free space has been observed near the wire. The conditions are complex, as there will be a layer of gas practically at rest near the hot wire, surrounded by gas in considerable movement due to convection. This limits, in effect, the extent of the temperature gradient, and consequently the thermal separation, to a small region round the wire. The increase in the width of the dust-free space obtained by reducing the air pressure is probably due to the reduced effect of convection, with a consequent extension of the temperature gradient. To obtain further progress, convection should be avoided as far as possible.

Professor K. G. Emeleus (*Belfast*) said: Useful information about the distribution of density in the gas near the hot body—and hence its temperature—also about the possible presence of local eddies in the convective streaming, would probably be obtained by using an interferometer.

Mr. A. G. Grant (*Darlington*) said: Prof. Whytlaw-Gray suggested in his introductory paper that the thermal precipitation phenomena might have a practical application to the industrial removal of dispersoids from gases. From the present discussion it seems evident that the dust-free zone breaks down for gas velocities much above zero. From this, it seems as though the phenomena cannot in fact find an industrial application; this being the case, will the authors explain what, apart from the evolution of the thermal precipitator for obtaining dust slides, is the object and value of this work?

Professor R. Whytlaw-Gray (*Leeds*), in reply, said: My reference in the introductory paper was not meant to suggest that thermal precipitation has at present any industrial applications. It is, however, of interest as it involves an effect which has hardly been studied and the explanation of which is still somewhat obscure. A closely related phenomenon is the deposition of particulate matter on cold surfaces from hot disperse systems. This too needs investigation.

¹ See references in *Proc. Physic. Soc.*, 1931, **43**, 142; see also T. L. Ibbs and A. C. R. Wakeman, *Proc. Roy. Soc.*, A, 1932, **134**, 613; P. H. Emmett and J. F. Schultz, *J. Amer. Chem. Soc.*, 1932, **54**, 378; 1933, **55**, 1376; and 1933, **55**, 1930; G. and O. Bluh, *Z. Physik.*, 1934, **90**, 12.

² S. Chapman, *Proc. Roy. Soc.*, A, 1928, **119**, 34; and *Proc. Roy. Soc.*, A, 1928, **119**, 55.

Mr. T. C. Angus (*London*) said: Should the downward air velocity in the thermal precipitator be not substantially greater than the natural upward velocity due to the convection currents from the hot wire?

Dr. R. Meldau (*Berlin*) said: If a hollow metal sphere of about 10 cm. diameter and pierced with fine holes is used as a condenser in a high tension field of 30,000 to 40,000 volts, and a fog or vapour cloud is forced through the holes, the fine particles take up to a very large extent a unipolar charge. Such an arrangement has been utilised by the firm Koerting of Hannover for inhalation apparatus and Dr. Wedekind, Cologne, reported upon experiments with it in the *Zeitschrift für Balneologie*, Sprüng, 1936, giving remarkable results.

Mr. C. F. Goodeve (*London*) (*communicated*): I think that a quantitative treatment of the dust-free space cannot satisfactorily be made until the experimental arrangement is such that convection is avoided completely and controlled temperature gradients are obtained. The fact that the dust-free space has the same thickness at points around most of the horizontal rod seems an unexpected coincidence. Apparently, the variation in velocity of the convection current exactly compensates the variation in thickness to be expected from the different times the particles are in the temperature gradient.

Bancroft's suggestions, referred to in this paper, that smoke particles are "sucked" in a temperature gradient cannot of course be taken seriously.

Dr. W. Cawood (*Leeds*), in reply, said: In answering criticisms regarding the small cylinders of radius of the order of the mean free path in which Knudsen's Laws (*i.e.*, $N_1 c_1 = N_2 c_2$) hold, I would like to point out that this is the fundamental assumption of the attempted explanation of the phenomena. Unless something of this kind is postulated one would expect a force even on objects of a much greater size, such as small vanes, etc. As far as I know, such forces are not obtained.

I will explain the idea of these small cylinders a little more fully. Imagine a cylinder about 1 mm. wide moving with a convection current. Then, considering only the movements of the molecules parallel to the axis of the cylinder, there will be mass movements of the gas in the cylinder, because the velocity at one side will be greater than at the other. As the radius gets smaller the difference of velocity will get less and it seems quite reasonable to suppose that in a cylinder of which the radius is of the order of the mean free path, there will be no difference of velocity and the cylinder of gas will move bodily in the convection current without mass movements inside it.

Mr. H. H. Watson (*Porton*), in reply, said: Sir Robert Robertson has referred to the deposition of dust on walls and the pattern staining on ceilings. Particles of smoke and dust in the air of a room are carried upwards by convection currents and are blown about in all directions by draughts. When these particles, often in quite rapid motion, are brought into contact with the walls, ceiling and furniture of the room they are deposited there, if the solid surface is cooler than the surrounding air.

For instance, there is usually a black deposit on the wall just above a hot water "radiator" or pipe. The convection currents bring many more particles into contact with the wall than does normal diffusion, and the conditions are right for deposition there. It is perhaps not so much due to a thermal force causing the particles to move down the temperature gradient on to the cool surface of the wall, as to the fact that the wall is not protected by a dust-free space.

The replica in light and shade on a ceiling of the construction in, and immediately behind, the plaster is a familiar sight, especially in industrial towns. When there is a wooden lath backing to the plaster, that part of the ceiling not backed by the laths is cooled by the air circulating above the ceiling, and dust can be deposited there. The laths insulate the remainder of the ceiling very efficiently, and dust cannot be deposited if the surface temperature is above that of the ascending air, because of the

protecting dust-free space. When the ceiling is backed by steel girders, as in the Chemistry Department of the University of Leeds, we have an inverse effect. That part of the ceiling backed by the girders is kept comparatively cool and a deposit is obtained there. To prevent pattern staining the temperature of the ceiling must be uniform over its surface. Work to attain this end has been done by Bonnell and Burridge.³

In rooms heated by direct radiation, as by an open fire, the walls and furniture are warmer than the air. They are thus protected by a dust-free space, and the dust in the air tends to remain in suspension, and is not deposited to the same extent as when the air is heated by convection, *i.e.*, by steam pipes or hot water "radiators," for then the air is usually warmer than the walls and furniture, and there is no protecting dust-free space.

In reply to Mr. Angus: If a thermal precipitator is supported alone in a dusty atmosphere, without a water aspirator or a source of suction, the convection stream from the wire pulls air upwards through the instrument at a rate which is so small that a very sparse dust deposit is obtained. This shows that the suction velocity is large compared with the opposing convection velocity.

In reply to Dr. Ibbs and Mr. Goodeve: I agree that much useful information would be obtained by studying the dust-free space when convection has been eliminated. We also want precise information about the variation of temperature within the first millimetre from a hot surface. For the practical application of the phenomenon, however, the space must be examined as it occurs in free air, and the empirical formulæ 5 and 6, which I have obtained, used.

³ D.S.I.R., *Building Research Bulletin*, No. 10 (H.M.S.O., 1931)

THE DETERMINATION OF SIZE DISTRIBUTION IN SMOKES.

BY H. S. PATTERSON and W. CAWOOD.

Received 10th February, 1936.

Smokes, unless dispersed under very special conditions which we have previously described,¹ consist of particles varying very considerably in size. The determination of the size frequency or size distribution, that is, the numbers of particles of different sizes present, is a matter of considerable difficulty. Generally speaking, the methods which have been attempted fall into three categories, firstly, those in which a simultaneous measurement is made of a number of particles suspended in air, secondly those in which some property of the particles is utilised to obtain separation of the various sizes, which can then be enumerated, and lastly those in which the smoke is allowed to sediment and an estimate made of the size frequency.

The first method is necessarily photographic, since it is impossible visually to estimate simultaneously a number of particles, and if they are measured successively, they tend to be selected rather than chosen at random. An ingenious photographic attempt was made by Wells and Gerke² who photographed the traces as seen in an ultramicroscope,

¹ *Proc. Roy. Soc.*, 1932, **136A**, 538.

² *J. Amer. Chem. Soc.*, 1919, **41**, 318.

in a stream of charged particles moving horizontally under photophoresis in a vertical alternating electric field. Each particle traverses a zig-zag path, by measurement of which its size can be deduced if its effective density and electric charge are known. Since there is considerable doubt as to both of these quantities the method cannot be used to give an accurate size distribution.

This method has been developed and improved by Fuchs and Petrianow³ who apply an alternating potential at right angles to the particles falling under gravity.

From the zigzag traces obtained photographically, both the charge and mass can be calculated and from the tracks of a large number of particles the size distribution can be obtained; this method can be used for particles of radius of 0.3μ but for smaller particles it is untrustworthy. Whilst for droplets this method is reliable, for aggregates such as are usually present in smokes, the evaluation of the effective density is difficult and hence the calculation of the radius from the mass is uncertain.

For coarse smokes we have attempted to photograph the vertical traces due to particles falling in the field of the ultramicroscope, but our results appeared to be of little value owing to the difficulty of avoiding convection currents.

The second method has been used by Rohmann⁴ who charged a narrow ribbon of particles by passing it through an ion stream and then precipitated the particles on to paper by means of an electric field. Under these conditions the charge caught by the particles is probably proportional to the square of their radius and hence on deposition separation of the various sizes should occur. This method has given good results with dust, but is unsatisfactory for the finer disperse systems. Regener,⁵ on the other hand, has suggested passing a smoke at varying velocities through a spiral, when particles above a certain size should be removed by centrifugal action, and counting the residue. In this case, the results would probably be vitiated owing to increase in the velocity of coagulation.

For particulate systems consisting of solid nonhygroscopic particles, sedimentation on to a slide, followed by microscopic measurement has frequently been used, and various types of sedimentation boxes in which a column of the smoke or dust is allowed to settle on to a microscope slide or cover glass, have been devised. The deposit is examined microscopically by transmitted light using an objective of high resolving power, and the particles are measured by an eyepiece micrometer. This method is both slow and laborious and, moreover, can only be applied to particles which are well within the limit of resolution of the microscope.

To overcome these difficulties we have carried out investigations along two lines.

(1) Photometric Method.

In this method, the deposit which in our experiments we obtained in a collector slide by means of the apparatus already described* was illuminated from the front to give a dark field as for counting. It was

³ *Koll. Z.*, 1933, **65**, 171.

⁴ *Z. Physik*, 1923, **17**, 253.

⁵ *Freundlich, Colloid and Capillary Chemistry*, 1922, 774.

* See page 1056.

then observed with a special eyepiece previously described.* containing an artificial particle. The brightness of the artificial particle could be varied by means of a neutral wedge and matched in brightness against individual particles in the deposit. In this way, if the law of scattering is known it is clearly possible to deduce the relative sizes of the particles, and divide up the total number into groups according to size. In practice the method proved somewhat laborious, but it is the only way available at the present time for investigating small particles. The most serious objection, however, is that the law of scattering varies considerably for particles having a radius in the neighbourhood of 10^{-5} cm., the index diminishing for homogeneous particles from the sixth power to the square of the radius with a comparatively small increase in size. For coarse smokes with particles well above this limit, the method should, however, be able to be applied easily. A typical coarse smoke is that obtained by burning magnesium ribbon and measurements have been made with this material. The law of scattering in this case has been previously measured over a fairly long size range¹ for particles suspended in the air, but since this smoke consists of loose complexes which on settling tend to flatten somewhat a further complication is introduced. The results obtained, though incapable of precise interpretation, showed clearly the progressive variation of size frequency as coagulation proceeded.

(2) Graticule Method.

By the examination of smoke deposits by direct light under the microscope using a high resolving optical system, it has been found possible,

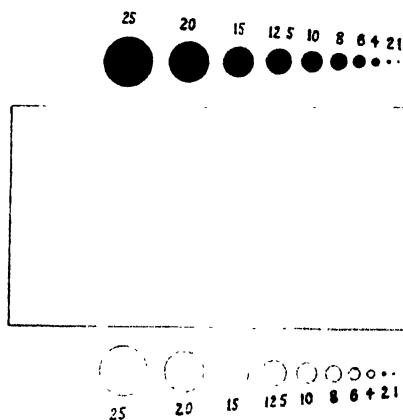


FIG. 1.

with the help of a specially designed graticule, to estimate rapidly the size frequency of particles ranging from about $1 \cdot 10^{-5}$ to $25 \cdot 10^{-5}$ cm. radius. A suitable deposit can be obtained in the very early stages of a smoke by using a collector slide holder* 2 mm. deep, and in the later stages 5 or 10 mm. deep, according to the number of particles. In practice for the graticule used a collector slide holder about 1 cm. deep gives a convenient density of deposit for a smoke containing about a quarter million par-

ticles per c.c. Instead of collecting the deposit in the usual way, the bottom collector slide is replaced by a brass plate carrying a No. 1 microscope cover glass. The brass plate in the collector slide holder is pulled in the ordinary way and after allowing time for sedimentation, the cover glass is removed and carefully mounted on a thin glass microscope slide. The optical systems which we have found best for obtaining the clearly defined images essential for satisfactory results consists of a 2 mm. apochromatic objective N.A. 1.40, used with a ($\times 12$) compensating ocular and a substage achromatic condenser of aplanatic aperture as near N.A. 1.0 as possible. There is no gain in using an oil immersion condenser, since the deposit is mounted dry. This combination gives a $\frac{1}{3}$ cone in the objective, which

* Patterson and Whytlaw-Gray, *Proc. Roy. Soc.*, 1926, 113A, 312

* See p. 1056.

is often considered to be the best working condition. As illuminant we have used a pointolite lamp together with a green or blue light filter.

The graticule, which is inserted in the focal plane of a ($\times 12$) compensating eyepiece, consists of a rectangle and a series of ten numbered circles and corresponding discs as shown enlarged in Fig. 1. These appear superimposed on the deposit as seen in the field of the microscope. The images of the circles and discs correspond in size to particles ranging from $1 \cdot 10^{-6}$ to $25 \cdot 10^{-8}$ cm. radius when the deposit is viewed with a 2 mm. Leitz apochromatic objective N.A. 1.40 and a tube length of 17 cm. The size of the rectangle under these conditions is $5 \cdot 10^{-3}$ by $2 \cdot 22 \cdot 10^{-3}$ cm. and for a different optical system the graticule can be standardised by measuring the dimensions of the rectangle with a stage micrometer. These graticules have been made to our design by Messrs. Rheinberg. The particles contained within the rectangle can be rapidly matched by eye against the discs or circles and their sizes determined. Since as a rule there are only about 6 particles in the rectangle, it is necessary to match a large number of fields, usually about 50, in order to obtain a good average. The numbers of the various sizes are noted down and a record is kept of the number of rectangles estimated. Since the area of the deposit corresponding to the rectangle and the depth of the collector slide holder are known, the number of particles per c.c. of the different sizes is easily calculated. The sum of the numbers per c.c. of all the sizes, gives, of course, the total number of particles per c.c. of the smoke. With a little experience the size

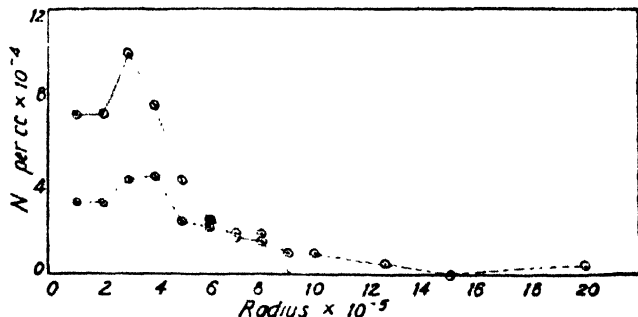


FIG. 2.

distribution may be estimated by this method both rapidly and accurately. If as a check a circle is occasionally superimposed on a particle by moving the mechanical stage, it will be found that the estimate of size is practically never in error. It may be noted that whilst with a coarse smoke all the particles will be seen and enumerated by this method, with a fine smoke the smallest particles are likely to be invisible and in this latter case the total number should be counted by the special ultra-microscope cell or the collector slide method.⁶ Actually, of course, the limit of visibility of small particles viewed by transmitted light, lies well below the limit of resolution. On this account, the smallest particles will all be reckoned as being of radius $1 \cdot 10^{-8}$ cm., whilst some of them may be below this size. It may be noted that the method can only be applied to non-hygroscopic particles of fairly high melting-point. It is not suitable for example for stearic acid, since the particles of this material tend to melt and spread due to the heat focussed by the condenser. Again, with loose aggregates such as the particles of magnesium oxide, an error may be introduced due to some flattening occurring on settlement. For the investigation of spherical particles such as those formed by the dispersion of certain dyestuffs or of fine dusts such as silica, the method is, however, reliable.⁷

Some results obtained with magnesium oxide smoke dispersed by

¹ Cp. Green and Watson, *Medical Research Council Report*, No. 199.

burning 6 ins. of ribbon in a cubic metre chamber are shown diagrammatically in Fig. 2. The more rapid disappearance with time of the smaller particles is evident. In this case only two deposits taken at 10 and 32 minutes from the start were counted.

The further application of this method should afford a means of tracing the change in size distribution during the life history of disperse systems in gases, provided the minimum size of particle is greater than 0.2μ radius.

THE COHESION BETWEEN SMOKE PARTICLES.

BY R. STEVENSON BRADLEY.

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The assumption is usually made that smoke particles will stick together on collision. With a liquid dispersion medium there is evidence¹ that this is not always true, and that a reverse may proceed at the same time as a direct coagulation. With smoke particles, however, reflexion after collision has not been observed, but a pair of particles often gyrate round their centre of gravity at what appears to be a slight distance apart. It is of interest, therefore, to study the conditions of temperature, size of particle, surface energy, etc., under which cohesion occurs with solid particles. In the case of liquid particles the lower energy consequent upon the formation of a large drop, due to decreased surface, will usually ensure coalescence, although the reverse occurs when a living cell breaks up into two units.

The cohesion between solid spheres has been derived theoretically by the writer,² and studied experimentally with quartz spheres. If we assume a very general law of force f between molecular centres,³ the cohesive force of attraction between two spheres of radii r_1 and r_2 is very nearly

$$F = 4\pi^2 q^2 \frac{r_1 r_2}{r_1 + r_2} \left[\frac{\lambda}{(n-1)(n-3)(n-4)(n-5)d^{n-5}} - \frac{\mu}{(m-1)(m-3)(m-4)(m-5)d^{m-5}} \right],$$

where $f = \frac{\lambda}{r^n} - \frac{\mu}{r^m}$, q is the number of molecules per c.c. and d the smallest distance between the centres of the surface molecules of the two spheres. Flattening of the spheres is not considered. The same assumptions, neglecting such refined considerations as the energy involved in the rearrangement of the surface molecules on the formation of a new surface, give for the surface energy of the solid⁴

$$\sigma = \pi q^2 \left[\frac{\lambda}{(n-1)(n-3)(n-4)(n-5)d^{n-5}} - \frac{\mu}{(m-1)(m-3)(m-4)(m-5)d^{m-5}} \right].$$

Hence
$$F = 4\pi \frac{r_1 r_2}{r_1 + r_2} \cdot \sigma \quad (1)$$

¹ Colloid Symposium Monograph, 1925, 2, 68.

² Bradley, *Phil. Mag.*, 1932, 13, 853.

³ Lennard-Jones, *Proc. Phys. Soc.*, 1931, 43, 461.

⁴ Bradley, *Phil. Mag.*, 1931, 11, 846.

The same value of d will appear in the expressions for F and σ if the surface molecules of the spheres are in contact at the point of contact. Equation 1 was subsequently derived by another method by Derjaguin.⁵

In practice it was found that F varied linearly with $r_1 r_2 / (r_1 + r_2)$ in the case of spheres of quartz and sodium borate.

These conceptions may be applied to the cohesion of smoke particles, since equation 1 is independent of the precise form of the law of force. The most obvious force tending to cause reversal of coagulation is the Brownian motion. Considering first the rotation, for a double particle formed from two spheres of radii r_1 and r_2 , we have $\frac{1}{2} I \omega^2 = kT$, where ω , k and T are the angular velocity, gas constant and absolute temperature, assuming that the double particle has the mean energy of rotation for the temperature concerned. If the density is ρ , $I = \frac{8}{15} \pi \rho (r_1^5 + r_2^5)$. The centrifugal force tending to cause disruption is

$$\frac{4}{3} \pi \rho \omega^2 (r_1^4 + r_2^4) = \frac{4}{3} \pi \rho \frac{1}{15} \cdot \frac{kT(r_1^4 + r_2^4)}{\pi \rho (r_1^5 + r_2^5)}.$$

Hence the point at which centrifugal overcomes cohesive force is given by

$$\frac{4}{15} kT \frac{r_1^4 + r_2^4}{r_1^5 + r_2^5} = 4\pi \frac{r_1 r_2}{r_1 + r_2} \sigma \quad (2)$$

This result is independent of the flattening which may occur on cohesion; the deformation differs markedly from that considered by Hertz for the case of two spheres pressed together, for then the pressure acts throughout the mass, whereas with cohesion only neighbouring layers of molecules are attracted towards one another. At the point at which centrifugal force overcomes cohesion the spheres are just about to part company, and there is no flattening, so that the above results are strictly true.

When $r_1 = r_2 = r$, equation 2 gives $r = \left(\frac{5}{7} \frac{kT}{\pi \sigma} \right)^{\frac{1}{2}}$. The cases of interest are approximately isomorphous solids, since with crystalline particles departure from the spherical shape will be serious. We should expect quite a low value of σ , about 30 dynes per cm. This gives for r a value of approximately 10^{-6} cm., *i.e.* all smoke particles of equal size will cohere. Even at 3000° r is only 5×10^{-6} cm. Hence the fact that equipartition is actually replaced by a Maxwellian distribution hardly affects the argument, since an infinitesimal fraction of particles will have sufficient energy of activation at room temperature. Disruption due to collisions will give similar results.

With particles of different sizes similar remarks apply. If $r_1 \gg r_2$ equation 2 becomes $\frac{10}{7} \frac{kT}{r_1} = 4\pi r_2 \sigma$. Hence $r_1 r_2 = 2 \times 10^{-16}$ at room temperature. A very small particle will cohere with a large one even if it will not do so with one of its own size.

Chains and aggregates of particles give similar results, *e.g.* with a linear chain of four particles breaking in the middle it can be shown that $r^2 = \frac{5}{54} \frac{kT}{\pi \sigma}$, which gives values of r smaller than before.

Although impossibly high temperatures would be necessary to obtain disruption with particles of the size usual in smokes, the velocities of the particles required is small compared with molecular velocities at room

⁵ Derjaguin, *Kolloid. Z.*, 1934, **69**, 155.

temperature, and the requisite velocity can be reached by violent fanning of the cloud, which sets up eddies, so that particles acquire relative velocity. A particle of density 2 travelling at 30 miles per hour will have sufficient kinetic energy to disrupt a stationary doublet of two particles each of radius 10^{-6} cm. if its radius is approximately 4×10^{-6} cm. With greater velocities (v) the radius of the heavy particle will be increased according to $v^{\frac{1}{2}}$; at 30 miles per hour a doublet of particles of radius 10^{-6} cm. requires a heavy particle of radius approximately 10^{-5} cm. for disruption. Cohesion in a large aggregate is confined to the separate cohesions between the component particles, and if one of these on the outside of a large complex were hit by another large complex with sufficient relative velocity disruption could occur. The medium may also impart rotational energy to complex particles, causing disruption. Hence for a violently fanned cloud the normal coagulation might be replaced by an approximately stationary state, owing to a rough balance between coagulation and disruption. Unpublished work of Dr. Colvin and the author working under the direction of Professor Whytlaw Gray showed that stationary states could be produced by violent fanning.

Coagulation in smoke proceeds partly because of the size of the particles. In actual practice the particles will be covered with a layer of adsorbed gas, but it is probable that the solids break through this at the point of contact. If this is not so, then the cohesion between the solids is still given by the same formula, but the distance d becomes d_1 and is no longer equal to the molecular diameter. Hence

$$F = 4\pi \frac{r_1 r_2}{r_1 + r_2} \sigma \left(\frac{d}{d_1} \right)^{m-5}$$

approximately, neglecting the repulsive term. To this must be added a term representing the cohesion of the two adsorbed layers. The latter may represent a repulsion if the adsorbed layers have, e.g. dipoles oriented perpendicular to the surface. A thin film of water could reduce the cohesion very considerably. When the coagulated particles are immersed in water they may be peptised, owing to the growth of the adsorbed layer. Wo. Ostwald and Haller⁶ have shown that the volume assumed by many colloidal precipitates is dependent on the dispersion medium, the thickness of the layer round a particle being about 1μ , and this effect is correlated with the dipole moment of the dispersion medium.

When the smoke particles are crystalline approximate calculations may be made. With two cubic particles of edge r face to face the cohesive force is approximately

$$F = \frac{\pi q^2 \mu r^2}{(m-1)(m-3)(m-4)d^{m-4}}.$$

Hence $F = \frac{\sigma}{d} r^2 (m-5)$. This gives results similar to those obtained with spheres.

⁶ Wo. Ostwald and Haller, *Kolloid Beih.*, 1929, **29**, 354.

THE SIZE-FREQUENCY OF PARTICLES IN MINERAL DUSTS.

BY H. L. GREEN.

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Dusts, in the colloid sense, may be classified as disintegration aerosols, and are formed by the release into the air of particles produced by the disintegration or disruption of solid matter. The term "dust cloud" is frequently used to distinguish the actual aerosol from precipitated or deposited dust. Dusts of mineral origin are of particular interest since they have given rise to an industrial problem of some considerable importance. Certain dusts containing silica, either free or combined or in both these states, when inhaled, cause silicosis and allied pulmonary diseases. Such dusts may be produced by the disintegration of rocks or minerals during processes involving crushing, grinding, drilling, blasting, or, in fact, during any process in which disruptive forces are applied to the material. One of the most important physical factors in the causation of pulmonary disease is the size of particles in the dusts, since only those particles below a certain size can reach the finer passages and air sacs of the lungs and start those changes leading to disease. A fraction of the particles which eventually reach the ultimate pulmonary tissue is deposited. It is probable that this deposition within the lungs is selective and particles of certain sizes are more readily retained than others. Furthermore, the harmful action of the particles after they have been deposited is probably dependent upon particle size. For the successful application of measures for the elimination of dust from air likely to be inhaled by workers, account must be taken of the sizes of particles. The design of exhaust ventilation must be such that the drag on the particles is sufficient to carry them out of the general atmosphere. In filtration of dust from the air, selectivity with regard to particle size plays a part, beside which, such factors as the rate of clogging of the filtering medium by particles of different degrees of fineness have to be considered.

The present investigation was undertaken primarily with the view to determining the sizes of particles likely to cause pulmonary disease, and is concerned with mineral dusts which form moderately stable aerosols mostly containing particles of mean diameter extending from about twenty microns downwards. Particles larger than this size have a high rate of sedimentation and are not considered to be of importance. Determinations have been essentially of an industrial character, but, as the results have thrown some light on the intrinsic nature of dusts, they are worth consideration purely from the standpoint of their bearing on general problems of the formation and behaviour of disintegration aerosols.

Method of Determining Size-Frequency.

Of the numerous methods available for the determination of particle size in aerosols, few are suitable for estimations under industrial conditions. Such methods as the direct estimation of size by measurement of the rate

of fall of particles, either visually or photographically, can only be readily applied in the laboratory. Reliance has, therefore, been placed on the microscopic measurement of the particles after they have been deposited from the dusts. This method is dependent upon the efficiency of the method for precipitating the particles and is limited by the resolving power of the microscope. For deposition, the thermal precipitator, modified from the original design of Whytlaw-Gray and Lomax, has been used.¹ In this instrument the particles are deposited on microscope cover-glasses on either side of an electrically heated wire. Dust-laden air is drawn into the instrument and the particles are deposited in linear streaks above the wire. Provided the rate of aspiration does not exceed 7 c.c. per minute and the wire is heated to a temperature such that the dust-free space surrounding the wire extends across the space between the cover-glasses, precipitation of all particles in the dust is complete between the limits of mean diameter of at least 20μ and about 0.2μ or smaller. In using the thermal precipitator samples may be taken over a period of time varying from a few minutes to several hours. Long period sampling is advantageous under industrial conditions since casual fluctuations in concentration and sizes of particles render samples, taken over a short duration of time, of doubtful statistical value.

The method of determining the size-frequency of particles has already been described in a previous publication¹ and need only be mentioned briefly here. After a sample of the dust has been taken with the thermal precipitator, the cover-glasses are ignited at 500°C . for about ten minutes in order to remove combustible or volatile particles of extraneous atmospheric pollution which are almost invariably present under industrial conditions. When cool, the cover-glasses are mounted dry on a microscope slide. Mounting in a liquid medium would tend to disturb the deposit and break up aggregates of particles which were present as such in the air. Although mounting in air enables the particles to be seen in maximum contrast to their surroundings, it has the disadvantage that it does not permit the fullest use to be made of the resolving power of the microscope.

Examination of particles is done under a magnification of 1500 diameters with a microscope fitted with a 2-mm. oil immersion apochromatic microscope objective and a $\times 17$ eyepiece. For rapidity of working, measurement of particles is made by means of a Patterson comparator graticule² set in the eyepiece, the sizes of particles being compared with the known apparent sizes of the discs of the calibrated graticule. It may be noted that a procedure, slightly different from that previously described, has been adopted for the present series of determinations. Instead of stating the diameter of each particle as being equivalent to that of the disc which it most nearly matches, particles have been grouped in small size ranges. According to this method all the particles above a certain size and up to and including another greater size are placed in one group. This enables the limits of size within various ranges to be defined more precisely than by the original method.

It should be emphasised that, owing to diffraction effects, exact measurement of particles below 0.4μ diameter is not possible with the microscope system employed, although the presence of particles 0.2μ diameter or smaller is readily detectable. It should also be noted that the particles, often irregular in shape, are treated as equivalent spheres and, in effect, it is the cross-sectional area of the two-dimensional image which is compared with the disc in the comparator graticule. If the particles are plate-like in form, the method may give rise to an over-estimation of sizes of particles, considered as spheres since such particles tend to be deposited with their larger surfaces parallel to the cover-glasses. When particles, such as those

¹ Green, H. L., and Watson, H. H., *Medical Research Council, Special Report*, No. 199 (H.M.S.O., 1935); Green, H. L., *Bull. Inst. Min. Met.*, No. 362, 1934.

² Green, H. L., *J. Industr. Hyg.*, 1934, 16, 29; Patterson, H. S., and Cawood, W., *this discussion* p. 1084.

of asbestos, have a pronounced fibrous form, it is better to make two distribution counts, one of the length and the other of the diameter of the particles.

Results.

Samples were taken in various industries which provided examples of sandstone, flint, hæmatite, shale, and asbestos dusts. The nature of the dusts will be described *seriatim* below, together with typical results for the size-frequency of particles. The size-frequency depends not only upon the nature of the dust, but on the precise conditions under which the dust is being formed, on the age of the cloud and on the distance from the source of production that the sample is taken. Owing to the existence of particles in dust clouds which have a relatively high rate of sedimentation, the size-distribution of particles is altering continuously with time. Thus size-frequency is very susceptible to changes in local conditions. It is not intended to describe in detail how size-frequency varies with different processes, but rather to give a general idea of size in relation to the nature of the dust producing material and the disruptive forces coming into play.

(a) **Flint dust**, produced in milling calcined flint (chalcedonic silica) containing about 90 per cent. silica.

Median diameter of particles: 0.8μ to 1.3μ ; 20 to 30 per cent. less than 0.5μ ; 70 to 80 per cent. less than 2μ ; 1 to 6 per cent. above 5μ .

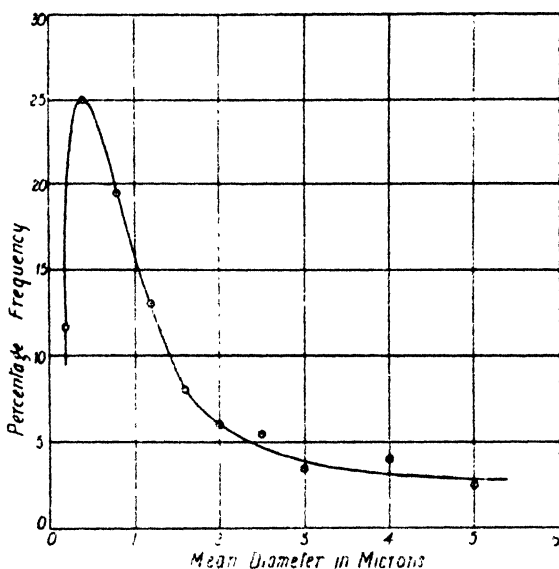


FIG. 1.—Size-frequency curve for particles in a sandstone dust.

(b) **Sandstone dust**, produced in shaping blocks of white sandstone by blows of a mallet on a cold chisel. This was a moderately fine-grained, highly felspathic sandstone containing subangular grains of quartz.

Median diameter of particles: 0.6μ to 1.1μ ; 25 to 45 per cent. less than 0.5μ ; 70 to 90 per cent. less than 2μ ; 1 to 8 per cent. above 5μ .

(c) **Hæmatite dust**, produced in blasting operations in a hæmatite mine; the hæmatite contained 80 per cent. of ferric oxide, 11.7 per cent. of silica, and 0.5 per cent. of alumina. Samples taken from one cloud only.

Median diameter of particles: 0.9μ ; 30 per cent. less than 0.5μ ; 82 per cent. less than 2μ ; 1 per cent. above 5μ .

(d) **Shale dust**, produced in drilling and blasting operations in a hard heading in a coal mine; a hard, close-grained shale containing 29 per cent. of free silica.

Median diameter of particles: 0.4μ to 1.2μ ; 25 to 55 per cent. less than 0.5μ ; 65 to 92 per cent. less than 2μ ; 1 to 10 per cent. above 5μ .

(e) **Asbestos dust**, produced in handling, disintegrating, carding and weaving asbestos. Samples derived from amosite, chrysotile and crocidolite varieties of asbestos have been examined.

Median length of fibres: 2.5μ to 3.5μ ; 8 to 15 per cent. less than 1μ ; 65 to 75 per cent. less than 5μ ; 87 to 90 per cent. less than 10μ .

Median diameter (thickness) of fibres: about 0.55μ ; 43 per cent. less than 0.5μ ; 82 per cent. less than 1μ ; 98 per cent. less than 2μ .

In addition to asbestos fibres in the samples, there was present about an equal number of ordinary dust particles derived from impurities in the asbestos. Various impurities are known to exist in asbestos, as mined, and may consist of talc, serpentine, magnetite and carbonates of calcium and magnesium.³ The size-distribution of these other mineral particles was as follows: Median diameter: 0.45μ to 0.8μ ; 30 to 55 per cent. less than 0.5μ ; 87 to 98 per cent. less than 2μ ; 1 to 4 per cent. above 5μ .

Detailed figures for certain specific samples are given in Table I. Fig. 1 shows a typical size-frequency curve for a sandstone dust, the sizes being determined in this case by the matching method and not by the grouping method.

TABLE I.—SIZE-FREQUENCY OF PARTICLES IN VARIOUS MINERAL DUSTS.

Size Group. (Microns).	Percentage Frequency for Various Dusts.				
	Sandstone.	Flint.	Shale (during Drilling).	Shale (after Blasting).	Hematite (after Blasting).
Up to 0.2	13.6	9.3	7.6	10.0	9.9
0.2- 0.4	14.3	15.7	13.6	10.5	14.7
0.4- 0.8	14.0	14.2	15.6	17.0	19.8
0.8- 1.2	11.3	13.0	10.6	12.5	17.6
1.2- 1.6	10.0	11.3	9.3	9.5	10.8
1.6- 2.0	8.0	9.6	8.0	6.5	8.6
2.0- 2.5	6.6	9.8	7.6	4.0	6.8
2.5- 3.0	6.6	8.2	7.0	10.0	4.8
3.0- 4.0	5.0	4.3	6.6	6.4	4.4
4.0- 5.0	3.3	2.5	3.6	4.6	1.8
5.0-10.0	3.6	0.9	3.0	4.0	0.8
Above 10	3.7	0.6	7.5	5.0	0.1

Discussion of Results.

The Sizes of the Particles.

Although the size-frequency of particles may show variations of a fairly large order between one kind of dust and another, the results have features which appear to be common to all kinds of mineral dusts. One particular feature is the high proportion of particles which are below 2μ diameter, and, in some cases, below 0.5μ . It is commonly believed that dusts contain a large proportion of relatively coarse particles. Gibbs⁴ distinguished between the various kinds of industrial aerosols according to the size of particles, and classified dusts as containing particles larger than 10^{-3} cm. (10μ) diameter, but later,⁵ in a modified classification, considered dusts to be disintegration aerosols containing particles greater in size than 10^{-5} cm. (0.1μ). The present results are in conformity with the latter classification and indicate that dusts possess a high degree of dispersion.

³ Hurlbut, C. S., and Williams, C. R., *J. Industr. Hyg.*, 1935, 17, 289.

⁴ Gibbs, W. E., *Clouds and Smokes*, London (J. & A. Churchill), 1924, p. 130.

⁵ Gibbs, W. E., *J. Soc. Chem. Ind.*, 1932, 51, 1042.

A comparable series of size-frequency determinations was made by Bloomfield⁶ in the United States by means of the Owens jet dust counter. Although his results show the same high proportion of particles less than 2.0μ diameter as in the present determinations, they show a very much lower proportion less than 0.5μ . In one case 10 per cent. less 0.5μ is recorded and in the remaining twelve cases the highest proportion is 3.0 per cent. These results are somewhat surprising, as it has been shown that the Owens jet dust counter is more efficient in precipitating particles of the order 0.5μ than those of 2μ diameter,⁷ and the types of dusts were not very different from those recorded in the present series of results. There is a possibility that some of the finest particles were not detected and measured, since the magnification of 1000 diameters used by Bloomfield was somewhat low for this kind of microscopy.

It is of interest to note that the finer particles in dusts cover the same size range as the coarser particles in smokes, which, in general, contain particles of diameter from 0.1μ to 1.0μ . Thus dusts of a high degree of dispersion are comparable with very heterogeneous coarse smokes. It may be noted, however, that fine dusts in an enclosed space have an apparently higher coagulation constant than heterogeneous smokes. The rate of diminution of particles with time follows approximately the law, $dn/dt = -Kn^2$, where n is the number of particles per unit volume at time t and K is a constant. Whytlaw-Gray⁸ gives values for the coagulation constant for heterogeneous ammonium chloride smokes ranging from 0.55 to 1.70×10^{-9} cm.³/sec. Whereas for flint dust clouds, containing particles not greater than 5.0μ diameter, values of the order of 6.0×10^{-9} cm.³/sec. were obtained by the author. These values were derived from counts by means of the ultramicroscope on the particles generated in a dust chamber. The high value of K is probably due to the extreme heterogeneity of the dust; furthermore, the process of coagulation is probably different from that in smokes and is due more to larger particles falling past the smaller ones and colliding with them than to collisions by Brownian motion. It may be noted that the samples of dusts in industry were for the most part taken within a short time of the release of particles which were being continuously generated, and, therefore, the samples were of the primary dust particles. In any case, the numbers of particles in dusts are, comparatively speaking, so low that the actual rate of coagulation is very slow. For instance, if the number of particles in the dust were 10,000 per c.c. (a high value) this would only diminish to about 8000 per c.c. after being left in an enclosed space for one hour, assuming that there were no loss of particles by sedimentation. Hence, aggregation by collision in dust clouds is not usually a factor of importance; such losses of particles that occur are due mainly to sedimentation. When aggregates are found in dusts, they are usually present as such in the original material from which the dust is generated. Re-dispersal of a dust that has been precipitated will often give rise to a cloud containing many aggregates.

A question of some importance is whether particles of diameter less than 0.2μ exist to any extent in dusts. An answer of this question has been attempted in several ways, although the results so far obtained are not sufficiently accurate to warrant their publication in detail. Particles generated by impact of a chisel on a block of sandstone in a dust chamber

⁶ Bloomfield, J. J., *U.S. Pub. Health Rep.*, 1933, 48, 961.

⁷ Green, H. L., and Watson, H. H., *loc. cit.*, p. 19.

⁸ Whytlaw-Gray, R., *J. Chem. Soc.*, 1935, 268.

were allowed to settle on collector slides,⁹ and were counted under a form of dark-ground illumination according to the method described by Whytlaw-Gray. These counts did not differ sensibly from those obtained by counting particles, which had settled on cover-glasses, with the direct vision microscope. The collector-slide method probably enables solid particles as small as 0.1μ diameter to be detected and counted.

Another method has been to count the sandstone particles by means of the photographic Aitken apparatus,¹⁰ which is capable of detecting particles well below 0.1μ diameter. In this case the difficulty has been to free the air from atmospheric nuclei which are revealed in the condensation process in the Aitken apparatus and which may far outnumber the dust particles in the air. This difficulty mainly arises when an attempt is made to reproduce an industrial process in a dust chamber of large volume. Again, so far, the results have not shown that particles below 0.2μ diameter exist to any appreciable extent in these sandstone dusts.

In certain determinations of size-frequency of mineral particles produced by blasting operations in coal mines, it was noted that there were large numbers of very fine particles which were just visible under the microscope and appeared to be rather smaller than the finest dust particles. Subsequent experiments with the explosive, when fired alone, showed that these fine particles were derived from the explosive itself and not from the rock, *i.e.*, they were incombustible smoke particles. Thus, even when rocks are disrupted with explosive violence, there is no indication that there are many particles formed which are less than 0.2μ diameter.

A point bearing on this question is that the size-distribution of particles in dusts tends to follow a probability law. It is true that at the top end of the scale there is a tendency to depart from the law owing to falling out of the larger particles before they reach the sampling apparatus, but, when losses due to sedimentation are not appreciable, the size-frequency curves approximate to asymmetric probability curves of the "cocked hat" type. Thus, distribution of sizes appears to be a purely random one; it may be inferred from the curves that the expectation of producing particles less than 0.2μ diameter is small.

On the theoretical side, Gibbs⁵ considered that there is a natural limit to the extent to which solids or liquids can be reduced in size by disintegration methods. This limit is imposed by the operation of cohesive or surface tension forces upon each separate fragment of material as it is being formed during the process of disintegration, and he considered the lower limit of particle size for such disintegration aerosols to be of the order of 0.1μ . Researches on the theory of fine grinding have yielded some information as to the limiting size of particle that can be formed by disintegration processes. In some work on this subject, Martin and his associates¹¹ did not find any end point to the production of fine particles, but as the smallest particles that were measured had a diameter of 0.85μ , the results of their experiments must be regarded as being inconclusive. On the other hand, Andreassen¹² estimated the sizes of particles by sedimentation in a liquid medium, and deduced that particles as small as 0.1μ diameter could be formed by grinding.

⁹ Whytlaw-Gray, R., *loc. cit.*, p. 270; Whytlaw-Gray, R., Cawood, W., and Patterson, H. S., *this discussion*, p. 1055.

¹⁰ Green, H. L., *Phil. Mag.*, 1927, 4, 1046.

¹¹ Martin, G., Blyth, C. E. and Tongue, H., *Trans. Ceram. Soc.*, 1923, 23, 61.

¹² Andreassen, A. H. M., *Kolloidchem., Beihefte*, 1928, 27, 349.

Mechanism of Formation of Dusts.

The size-frequency of particles throws some light on the mechanism of the formation of dusts. The process of disintegration of the mineral or rock is accomplished by the application of shearing and tensile stresses, slowly, as in milling processes, or suddenly, as in drilling with pneumatic drills. The effect of the applied forces is to cause disintegration by splitting or cracking along planes of weakness in the material. It is possible to distinguish between two classes of particles, represented respectively by small fragments, and by fine particles released from the freshly formed surfaces by cracking on a micro scale as the material is torn apart. It is likely that the dusts which were estimated in the present series of experiments belong almost wholly to the latter class. On this theory it is possible to account for the observation that the sizes of particles in dusts formed by explosions are comparatively little different from those of particles formed by less violent processes of disintegration. Explosion entails disruption with extremely high velocity, but in essentials the action is the same as in other disintegration processes, that is, fragmentation takes place with release of fine particles from freshly exposed surfaces. It is true that fragmentation is more complete, but the sizes of the finer particles are similar to those of other industrial dusts.

It would be expected that the size and shape of dust particles would depend upon the mineralogical nature and structure of the material from which they are derived. With the exception of the case of asbestos, the present series of results cannot be regarded as being significant in providing information in this respect. There were so many local factors influencing the samples, that it would not be safe to draw more than generalised conclusions from the estimation of size-frequency. Asbestos, however, provides an example of a mineral in which there are definite planes of cleavage, and the splitting process takes place along these planes, yielding fine fibrous particles.

In the case of rocks containing several minerals of different hardness and crystal size, fracture may occur more readily through some of the minerals than through others, and the composition of the dust may be different from that of the original rock. The results so far obtained have not yielded any real information as to the selective fracture of the different mineral constituents. One difficulty in the way of determining the nature of the dust particles in relation to the nature of the parent rock is that such a high proportion of particles are less than 2μ diameter and, at present, there is no physical method available for identifying the exact nature of individual particles of that size range.

Summary.

Samples of industrial mineral dusts have been obtained by means of the thermal precipitator, and the size-frequency of the particles determined under a microscope of high resolving power. Data for the size-frequency of particles derived from flint, sandstone, hæmatite, shale and asbestos are given. It was shown that most of the particles are smaller than 2μ diameter, but there was little evidence that particles of less than 0.2μ diameter occur in mineral dusts. The dusts are considered as disintegration aerosols of a high degree of dispersion, and the significance of the results has been discussed on this basis. A theory of the mechanism of the formation of dusts has been put forward.

The author is indebted to Mr. H. H. Watson for his co-operation in obtaining samples of the dusts. He is also indebted to the Industrial Pulmonary Disease Committee of the Medical Research Council, on whose behalf this work was undertaken, for permission to publish this paper.

GENERAL DISCUSSION.*

Dr. K. Söllner (*London*) said: Can Mr. Green throw some light upon a closely related problem, which may, I believe, be noticed fairly regularly in clean country fogs, and in the presence of fine, clean stone dust, even after blowing it through a hot flame. The presence of a badly stoppered bottle of $\text{Fe}(\text{CO})_5$ in a room may also produce a similar sensation. The odour seems to be fairly independent of the nature of the disperse phase, provided that the latter is chemically inert and that no foreign odorous substances are present. The only very tentative explanation I can so far offer assumes that very fine particles reach the olfactory organ high up in the nose (quite analogous to the case mentioned by Green), and adsorb or dissolve some substance naturally present there: this disturbance of the natural stationary state in the olfactory organ possibly causing a sensation of smell.

Dr. C. G. Addingley (*Cleckheaton*) said: I have been using a method somewhat similar to that described by Green, for estimation of asbestos dust in the atmosphere of an asbestos factory; an Owens' jet dust-counter was used, and the cover-glass ignited to remove organic matter. In smoky districts a visible ash deposit is left by the soot particles on the cover-glass after ignition; the number usually varies between about 30 and 150 particles per c.c., but counting is somewhat difficult and uncertain, as the particles are of about the minimum size which the microscope will resolve. The average size of the asbestos particles varies naturally with the process to which the asbestos is being subjected but, in the measurements I have taken, it is much smaller than that given in the paper. I have always found 50 per cent. or more of the particles 0.5μ or less, 5 to 25 per cent. between 0.5 and 2μ , 2 to 10 per cent. between 2 and 5μ , and up to 5 per cent. over 5μ .

Dr. R. Lessing (*London*) said he could not agree that the size of particles in dusts formed by explosions differed little from that of particles formed by less violent disintegration. In experiments in a Welsh anthracite mine to study the incidence of silicious dust in various mining operations, he found that the dust produced by drilling the hard shale settled relatively quickly, whilst that released by shot-firing in the same rock remained suspended very much longer. He attributed this to differences in particle size. The dust counts in the air were made with a konimeter, and he admitted that in this instrument particles below a certain size, say 0.5μ were not observable.

Professor K. G. Emelius (*Belfast*) said: It would be interesting to attempt to find some correlation between the size frequency in dust formed by shattering of crystalline material, and the size frequency in the secondary structure of the crystal shattered. Might there not be a tendency for the dust particles to be the actual secondary units in the original substance?

Professor E. N. da C. Andrade (*London*) said: The words "mosaic" and "secondary structure" have been used in many different senses, and made to include, for instance, the slight changes in inclination which occur at small intervals on the surface of rock salt, and certain other, crystals. There seems no reason why these changes of direction should be sources of weakness, for in general, the more perfect a crystal, the weaker it is, and polycrystalline materials, where the changes of direction are large,

* On the three previous papers.

are very strong. A system of actual minute cracks, such as those found in diamond, has also been called a mosaic structure, and in such cases it seems highly probable that the cracks should be places of weakness, and that the material should tend to fracture along them. I do not know what evidence there is for this type of structure in crystals which have been studied in the pulverised state, but Professor Emeleus' suggestion might with profit be followed up experimentally.

Mr. F. I. G. Rawlins (*London*) said: The problem of measuring small particles might be facilitated by using a microscope similar to that developed by Barnard. Ultra-violet light is used, and the optical system is quartz or fluorite. It is clear from the Abbe-Rayleigh equation that high numerical aperture is essential and objectives having this feature are now available.

Dr. F. T. Peirce (*Manchester*) said: Has any systematic work been done on the efficiency of filtering as a function of pore and particle sizes? This might yield a possible, though hardly a precise, method of determining size distribution, and is of direct interest to questions of filtering, including the retention of dust in the nose.

Mr. A. Dooley (*Birmingham*) said: Has the X-ray powder diffraction method been considered as regards its application to the identification of the constituents of dust and smokes? In my experience, the method is satisfactory for particles at least as small as 0.5μ .

Dr. W. Cawood (*Leeds*), in reply, said: Dr. Dobson has asked a question about the different laws of scattering of light by small particles mentioned briefly in this paper. The subject is treated in some detail by Whytlaw-Gray and Patterson in *Smoke* (E. Arnold & Co.), chap. xiii. Briefly, Rayleigh¹ showed that for infinitely small particles the law was $I \propto r^6$, where I is the intensity of the scattered light and r is the radius of the particle. Mie² has shown mathematically that for particles of diameter greater than one-tenth the wavelength of the incident light, the power will decrease with increase of radius to slightly less than two and will then increase to two when the particle is large enough to become a true reflector. Jobst³ has extended Mie's theories and simplified them. Patterson and Whytlaw-Gray⁴ have obtained confirmatory experimental proof.

Mr. R. S. Bradley (*Leeds*) (*communicated*): In the grinding of particles mentioned in Green's paper, the work required to overcome the cohesion, and separate a crystallite into two parts, decreases as the size increases, but the work per gm. of material increases rapidly owing to the increasing number of particles. There is an increase in the work required for the disintegration of particles of diameter less than approximately 10^{-4} cm., owing to the secondary structure of the solid (lineage or mosaic structure), involving the presence of pores and cracks. The energy of a "crack surface" is roughly half the true surface energy of the solid, on which depends the work required to disintegrate a perfect crystal, so that further decrease in size after the destruction of the secondary structure, requires a marked increase in work. This may well set a limit to the size of particles obtained by grinding a solid.

Mr. H. L. Green (*Porton*) in reply, said: The phenomenon to which Dr. Söllner has referred, must, I think, be associated with the filtration of fine particles in the passages of the nose, and I imagine that the explanation offered by him affords a tentative solution of his problem. Possibly the familiar earthy smell after a light shower of rain in summer may be caused by the impact of the raindrops on the dusty ground and the release into the air of fine dust particles which are subsequently trapped in the nose. It may be that the solubility of these seemingly chemically inert substances in the tissue fluids is sufficient to cause a sensation of smell.

The discrepancy between the general trend of Dr. Addingley's results

¹ *Phil. Mag.*, 1871, 41, 107, 441.

² *Ann. Physik*, 1908, 25, 377.

³ *Ibid.*, 1925, 76, 863.

⁴ *Proc. Roy. Soc., A*, 1926, 113, 312.

for asbestos dusts and that of mine would appear to be due to differences of method. In the report written by Watson and myself for the Medical Research Council,⁵ we gave the results of the tests on the efficiency of various dust sampling instruments, and showed that, for flint dust, the Owens jet dust counter only precipitates about 40 per cent. of the particles, and is apparently more efficient for the *smaller* particles than the *larger* ones. I have not checked the efficiency of the Owens counter for asbestos, but the accuracy of the results with the thermal precipitator has been confirmed by parallel determinations by a sedimentation method on asbestos dusts generated in a dust chamber. In the particular works where the asbestos samples were obtained, the smoke particles, after ignition, left no residual ash, but such ash particles were noted in dusts determinations in other places, especially at Sheffield.

The experience of Dr. Lessing also differs from mine, but as his findings are based on visual observations on rates of settling which, in my opinion, may give rise to misleading conclusions and, on counts with the konimeter, which gives results of doubtful absolute or even comparative value, I do not think they can be regarded as disproving the validity of my own conclusions. It would be of interest if thermal precipitator samples could be taken in the mines where Dr. Lessing made his experiments.

Professor Emeleus has raised a most interesting point which I hope will be followed up by further investigation of the secondary structure of crystals. The remarks of both Professor Andrade and Mr. Bradley also lend support to the view that the size-frequency of the particles may be related to the secondary structure of the crystals from which they are derived.

I have at various times considered using the ultra-violet microscope, as suggested by Mr. Rawlins, but I decided that, unless it is shown that there are in dusts numerous particles below 0.2μ diameter, the gain in accuracy by using an ultra-violet microscope would not compensate for the loss of the speed and general utility of the ordinary visual microscope.

Dr. Peirce raises a question which has hitherto received but little attention, although some theoretical work on it has been done by Albrecht,⁶ and it was discussed by Gibbs in his book on *Clouds and Smokes*. The subject is of obvious importance, especially in connection with the protection of workers against harmful dusts by means of respirators, and the general problem of the filtration of dusts in industry. I am doubtful whether filters would be sufficiently selective in their action to enable them to be used for the accurate determination of size-distribution of aerial dispersoids.

In reply to Mr. Dooley, the X-ray powder diffraction method has been used for the determination of the percentage of free silica in rock dusts, notably by Clark and Reynolds⁷ in Canada, but the method appears to be limited at present to one or two constituents of the dust.

⁵ *Medical Research Council, Special Report*, No. 109 (H.M.S.O., 1935).

⁶ *Physikal. Z.*, 1931, **32**, 48.

⁷ *Univ. Toronto Studies, Geol. Ser.*, 1935, No. 38, 13.

THE AGGREGATION OF SUSPENDED PARTICLES IN GASES BY SONIC AND SUPERSONIC WAVES.

BY O. BRANDT AND E. HIEDEMANN.

Received 9th March, 1936.

New optical methods for rendering sonic and supersonic waves visible have been systematically studied in the last four years.¹ O. Brandt and H. Freund² tried, *inter alia*, the addition of tobacco smoke to indicate the wave-length of sound waves of frequencies between 6 and 50 k.c. in air enclosed in a tube; they observed an almost instantaneous precipitation of the smoke, the rapidity of which was the more astonishing as other observers of the coagulation of smoke by supersonic waves of lower frequency (e.g., H. S. Patterson and W. Cawood³) found only very much smaller effects. We thought, therefore, that further studies on the process of rapid precipitation should be of interest.

Photomicrographic and Kinematographic Observations.

The nature of the process was not immediately evident. Microscopic observation showed suspended particles of some size; this proved that aggregation had taken place in the sound field. More information was secured when photomicrograms of the suspended particles were obtained. The use of kinematographic methods yielded especially significant results. In these experiments it was necessary to obtain photomicrographs with very short times of exposure ($1/125$ second) in order to distinguish between that movement of the particles due to the general circulation between node and anti-node and that due to the oscillation. This was accomplished with the optical arrangement shown in Fig. 1. S represents the end of vibrator rod. R is a vertical sounding tube containing air to which tobacco smoke was added. An observation chamber K made from two ordinary cover-glasses sealed to a celluloid frame of 0.7 mm. thickness was fixed on the bottom of R. Light from an electric arc L was concentrated by a condenser K₀, a diaphragm B serving to screen the central rays. The aperture of the objective of the microscope must be the same as that of the rays screened by the diaphragm, so that no direct light, but a maximum of the light diffracted by the suspended particles, can enter the microscope.

¹ E. Hiedemann, *Naturw.*, 1935, **136**, 337; *Z. Physik*, 1935, **96**, 273; *Ergebn. exakt. Naturwiss.*, 1935, **14**, 201; E. Hiedemann, H. R. Asbach and Ch. Bachem, *Nature*, 1934, **133**, 176; *Z. Physik*, 1934, **87**, 734 and **88**, 395; E. Hiedemann, H. R. Asbach and K. H. Hoesch, *Naturwiss.*, 1934, **22**, 465; *Z. Physik*, 1934, **90**, 322; E. Hiedemann and Ch. Bachem, *Z. Physik*, 1934, **89**, 502 and **91**, 418 and 1935, **94**, 68; E. H. Hiedemann and E. Grossmann, *Z. Physik*, 1935, **95**, 383; E. Hiedemann and K. H. Hoesch, *Naturwiss.*, 1935, **23**, 511, 577 and 705, and 1936, **24**, 60; *Z. Physik*, 1935, **96**, 268 and **98**, 141; E. Hiedemann and N. Seifen, *Z. Physik*, 1934, **91**, 413; Ch. Bachem, *Z. Physik*, 1934, **87**, 738; H. Falkenhagen and Ch. Bachem, *Nature*, 1935, **135**, 830, *Z. Elektrochem.*, 1935, **41**, 570.

² O. Brandt and H. Freund, *Z. Physik*, 1934, **92**, 385, and 1935, **94**, 348 and **95**, 415; *Z. physik. u. chem. Unterr.*, 1935, **48**, 259; *Blätter Untersuchungs- und Forschungs-Instrumente*, 1935, **9**, 57.

³ H. S. Patterson and W. Cawood, *Nature*, 1931, **127**, 667.

Fig. 2 represents the circuit of the vibration generator. The vibrator rod (made of Indilatans-steel) was initially magnetised by means of the coil L_1 carrying direct current. Fig. 3a gives a photomicrograph of the

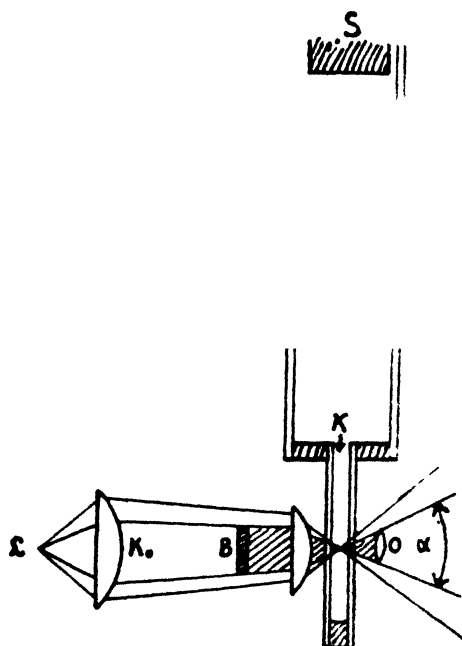


FIG. 1.—Photographic arrangement.

particles immediately after the generator begins to work; the particles are oscillating under the influence of the sonic waves and appear therefore as small streaks with more intensive ends. The length of the streaks is determined by the amplitude of oscillation of the particles.⁴ The time of exposure was $1/125$ sec. Fig. 3b shows the particles half a second later; the particles of the smoke have in the meantime become so much enlarged by aggregation that their inertia inhibits noticeable oscillation. The time of exposure for this photomicrograph was $1/10$ sec. so that the tracks of the moving particles are marked. The coalescence of two or more streaks shows the continued coagulation.

Fig. 4 shows a series of photomicrographs selected from kinematographic observations. Fig. 4 (a) shows the suspended particles before the sonic waves are produced; Fig. 4 (b) taken immediately

after switching on the generator, the oscillation of the particles is observed. Figs. 4 (c) to (f) show different phases of the process. Figs. 4 (g) and (h) were made after disconnecting the generator. A comparison of these last

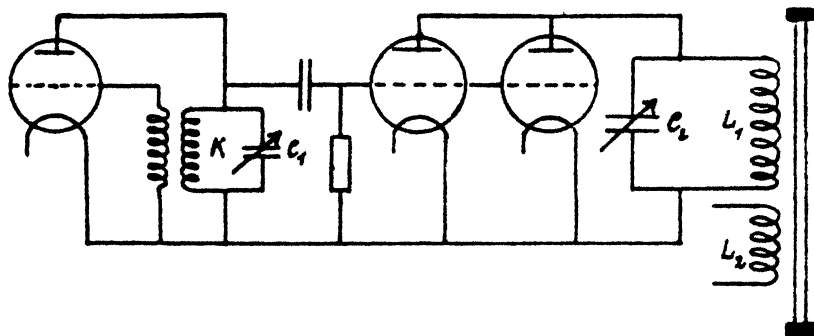


FIG. 2.—Vibration generator circuit.

two pictures with the first indicates the increase in size of the particles. The time of exposure for each picture of the series was $1/25$ sec. Whereas the non-coagulated particles practically remain at the same place during that time (they are photographed as points), the coagulated particles cross nearly the whole range of vision.

⁴ E. N. da C. Andrade (*Physic. Soc., London, Report of a Discussion on Audition*, 1931) first pointed out the possibility of measuring the intensity of the sound field by the amplitude of the oscillating particles.

These and many other photographs, as well as supplemental subjective microscopic observation, led us to distinguish two principal phases of the process. In the first phase the particles oscillate under the influence of the sound waves and take part in the general circulation between node and antinode, increasing in size by aggregation which takes place in the sound field owing to collisions of the particles. In the second phase the particles are so much enlarged, that they no longer oscillate, but describe very complicated and irregular tracks, similar to those observed by Andrade with particles of cork at lower frequencies.⁶ During the second phase the process of coagulation continues by collisions between the enlarged particles and also between enlarged and still oscillating particles.

Measurements of the Rate of Increase in Size of the Particles.

The extent of the increase of the size of the particles under the influence of the sound field was determined by different methods. The measurement of the velocity of the falling particles gives accurate information on the mass of the particle in the case of spherical particles if the Stokes - Cunningham formula is used; if the particles are not spherical the information so obtained is less reliable, but in most cases gives the order of magnitude. In view of the aniso-dispersity of the aerosols we only measured the velocities of the largest or most rapidly falling particles; the results of the measurement do not constitute therefore an average of the rate of enlargement, but are none the less significant.

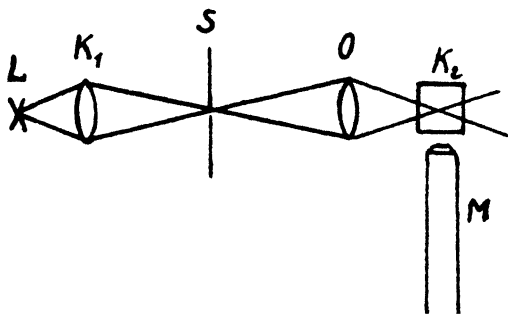


FIG. 5.—Optical arrangement (S. and Z.).

Of course, the range of vision must be sufficiently large for the observation of a considerable number of falling particles, so that the identification of the largest particles does not offer any serious difficulties. For various reasons the observation chamber and illumination applied in the photographic work could not be used. The optical arrangement of H. Siedentopf and R. Zsigmondy (Fig. 5) seemed to be most suited for these measurements. The objective O projects a reduced image of the slit S into the observation cell K_2 . The space traversed by the falling particles was well defined by two horizontal threads in the microscope. To avoid disturbances by currents of air in the observation chamber a special double cell K was used (see Fig. 6). The falling particles enter the cell K_1 . The illuminating band of light passes first through the window F, which is covered by a glass G_1 , into K_1 and then through the glass G_2 into the chamber K_2 , where it is absorbed at the opposite blackened wall. In the direction of observation the cell is covered by a cover-glass. All walls which could cause disturbing reflections are suitably blackened. Fig. 7 shows how the observation cell is fixed to the sounding tube.

As it was desirable to measure many particles successively the time of fall was registered by a Morse apparatus. The Morse-key was pressed as long as the particle moved from the upper to the lower thread in the microscope. The time could be determined from the registered lines with great accuracy by a simple arrangement which printed marks on the same

⁶ E. N. da C. Andrade, *Phil. Trans.*, 1932, **230A**, 413; *Proc. Roy. Soc.*, 1931-32, **134A**, 445.

paper at regular and known time-intervals. The different intensities of the sound field could be compared by measuring the amplitude of oscillation of the end of the vibrator rod. This was done by adjusting a microscope to an illuminated point on the surface of the end of the rod, when the rod is oscillating the point appears as a line, the length of which can be determined by a micrometer in the eye-piece of the microscope.

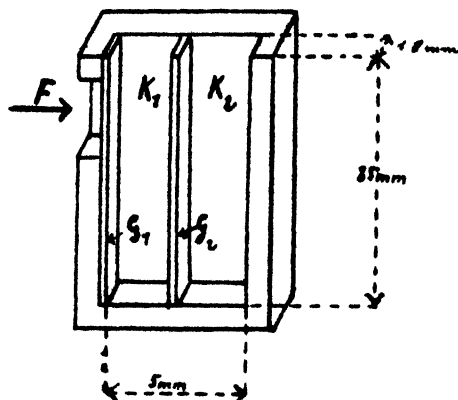


FIG. 6—Observation chamber

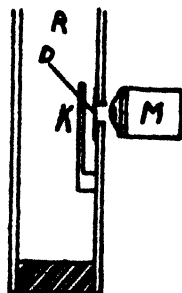


FIG. 7—Sounding tube

Table I shows the relationship of the increase in size to the sound intensity, the first column gives the amplitude of the oscillating rod, the other column the ratio of the increased mass m to the initial mass m_0 of the particle. In each experiment the aerosol (tobacco smoke) had been under the influence of the sound waves for a time of 5 seconds. Higher intensities of sonic waves were intentionally not used for the measurements. The data of the last column were calculated by the Stokes-Cunningham formula. As to the deviation of the coagulated particles of tobacco smoke from spherical shape see below.

TABLE I

Amplitude of the Vibrator Rod in mm	Ratio of the Increased Mass m to the Initial Mass m_0 , (m/m_0)
0	1
9×10^{-2}	2.1
18×10^{-2}	8.7
36×10^{-2}	13.6
54×10^{-2}	200

TABLE II

Time Elapsed after Connecting the Generator in Seconds	Ratio of Increased Mass m to Initial Mass m_0 , (m/m_0)
1	4
2	13
10	110

More reliable results may be obtained by using an aerosol in which liquid (and therefore strictly spherical) particles are suspended. By dispersing paraffin oil a fog was produced, the concentration of which was only 1/7 of that of the tobacco smoke used. Table II represents some results obtained with this aerosol, and shows how the increase in size depends upon the length of the time during which the sonic waves operated on the system. In all measurements the amplitude of the vibrator rod was 36×10^{-2} mm.

The dependance of the increase in size of the particles upon the intensity (Table I) proves that with increasing intensity the process may be expected to be highly efficient. Such experiments were successfully made

ERRATA.

This volume. Figs. 3a and 3b after page 1104 : For *size* read *amplitude*.
(Cf. page 1123 where *diameter* is stated.)

Page 1105 (last words) : For *geometrical shapes* read
geometrical shade (*geometrischer Schatten*).

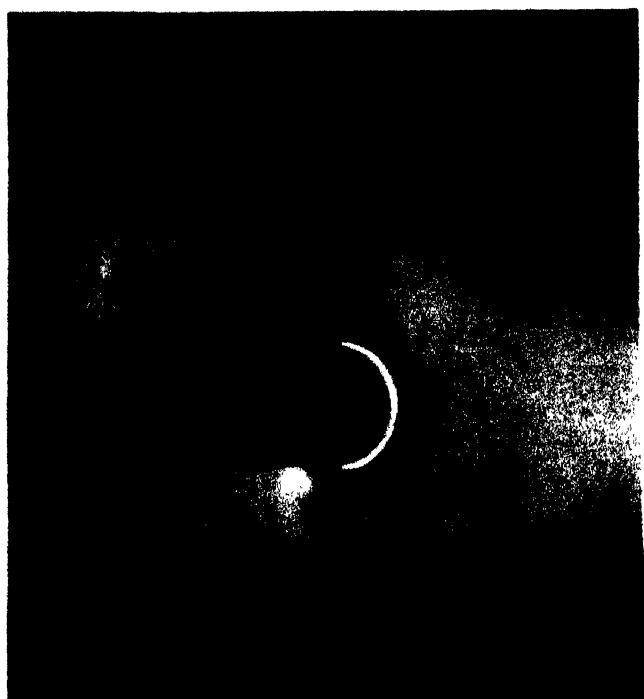


FIG. 2. Photograph of dust-free space surrounding a hot rod in sulphur smoke. Inner very dark portion is true dust free space. Secondary semi-dark space is due to evaporation effect referred to on page 1075.

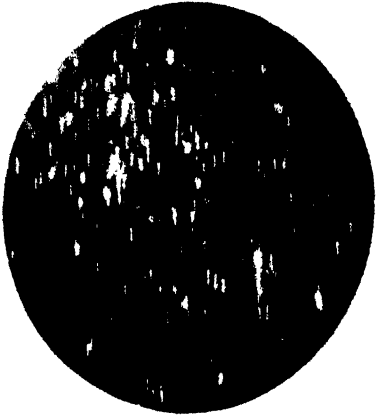


FIG. 3a.

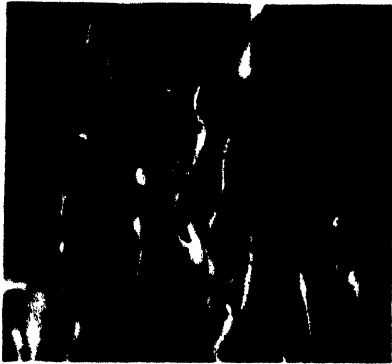


FIG. 3b.

Frequency, 10 kc

Size of oscillating particles. Fig 3a
 ~ 0.015 mm ; Fig 3b, ~ 0.045 mm

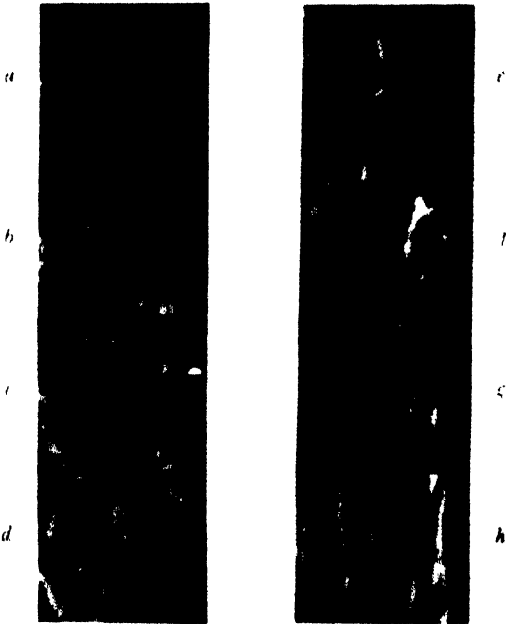


FIG. 4.

[See page 1102.



FIG. 11.—Tobacco smoke.

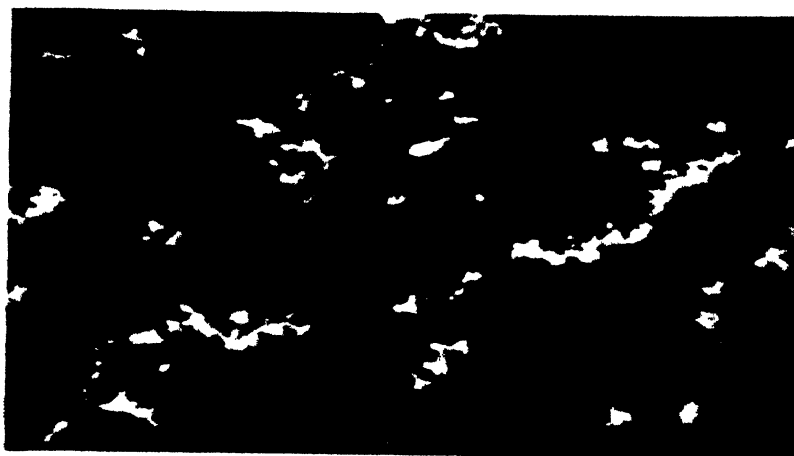


FIG. 12 -- NH_4Cl (after).

($\times 70$)

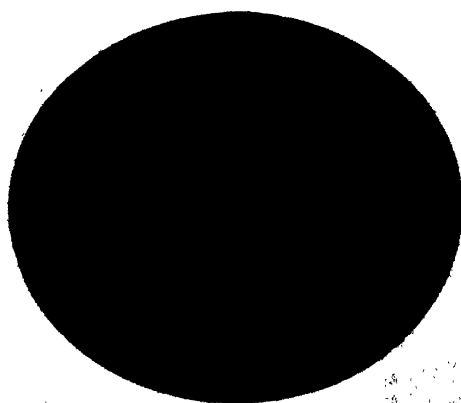


FIG. 13 -- NH_4Cl (before).

($\times 70$)

[See pages 1107 and 1108.

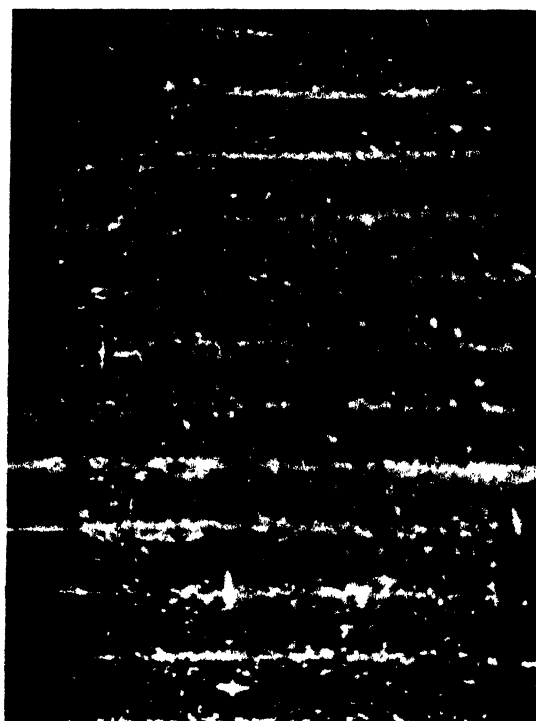


FIG. 1. MgO

[See page 1111

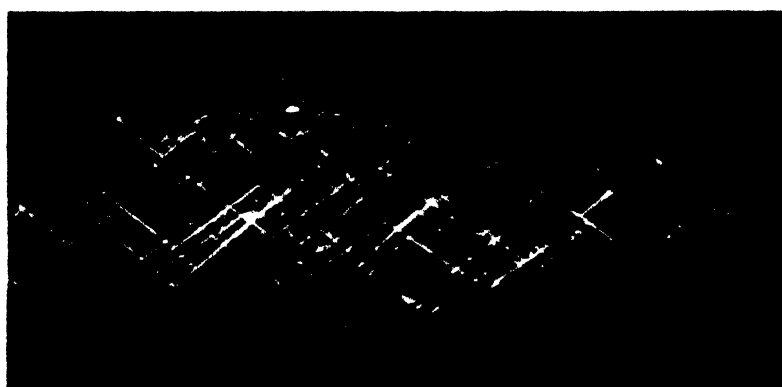


PLATE 1.

[See page 1135.

by means of the air-jet-generator and a powerful magnetostriction-generator and are described below.

Optical Measurements.

Whereas the above measurements give information only as to the increase in size of the largest particles present, one may obtain results as to the average by using nephelometric methods. The high aniso-dispersity which is rapidly brought about under the influence of the sound waves permits only somewhat rough results. Since increase in size under the influence of the sound field is a rapid process, it is necessary to use an arrangement allowing a record of instantaneous changes of the optical properties (the absorption of light) of the aerosol. This condition could be realised by measuring the intensity of light with a photo-electric cell connected to a Galvanometer (Moll) of a very short period of oscillation (1/50 sec.). The deflection of the galvanometer was recorded on a rotating film. The absorption was measured by applying a differential circuit containing two photo-electric cells, represented by Fig. 8. Light from

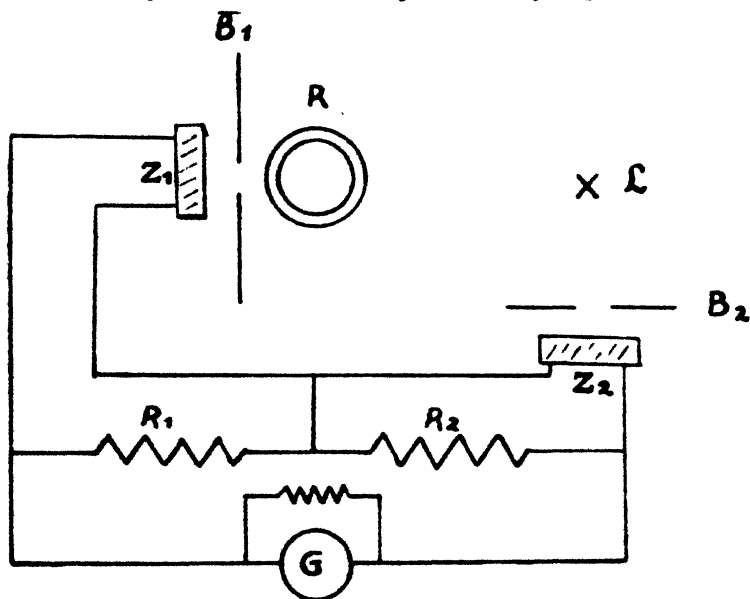


FIG. 8.—Circuit for Nephelometric measurement.

the source L is made parallel by a large (150 mm. diameter) lens (not shown in the Fig.) and then caused to traverse the sounding tube. A similar lens (not shown) forms an image of the source on the diaphragm of the photo-electric cell. A broad beam of light was chosen in order to have several nodes and antinodes in the observed region and to eliminate the influence of local air currents. From the same source, L , light also enters the photo-electric cell Z_2 through the diaphragm B_2 , which has a variable aperture. The electric differential circuit is so simple that it needs no explanation. The aperture of the diaphragm B_2 is varied until the galvanometer gives no deflection when there is no aerosol in the tube. When aerosol is brought into the tube the galvanometer deflection increases with increasing absorption of light. By means of neutral tint glasses (the absorption of which was well known) it could be shown that the deflection of the galvanometer was proportional to the absorption of light.

The absorption of light by suspended particles of large size can very approximately be calculated if one considers only the geometrical shape

of the particles which are supposed to be opaque.⁶ The coefficient of absorption is then given by $n \cdot q$, if n is the particle-concentration and q the cross-section of a particle. O. Werner⁷ has experimentally proved that this theory of G. Mie gives very satisfactory results when applied to evaluate practical measurements. Using the assumptions of Mie he derives the following formula for the extinction E of light:

$$E = n \cdot \pi \cdot r^2 \cdot \pi \cdot s \cdot \log e \quad (1)$$

where s is the length of the path of the light in the aerosol and r the radius of a suspended particle. For a constant value of r the extinction E is proportional to the particle-concentration. To obtain the increase in size of the particles by absorption measurements, we must consider that the radius r changes with n . If the mass-concentration ($g./cm.^3$) at least remains

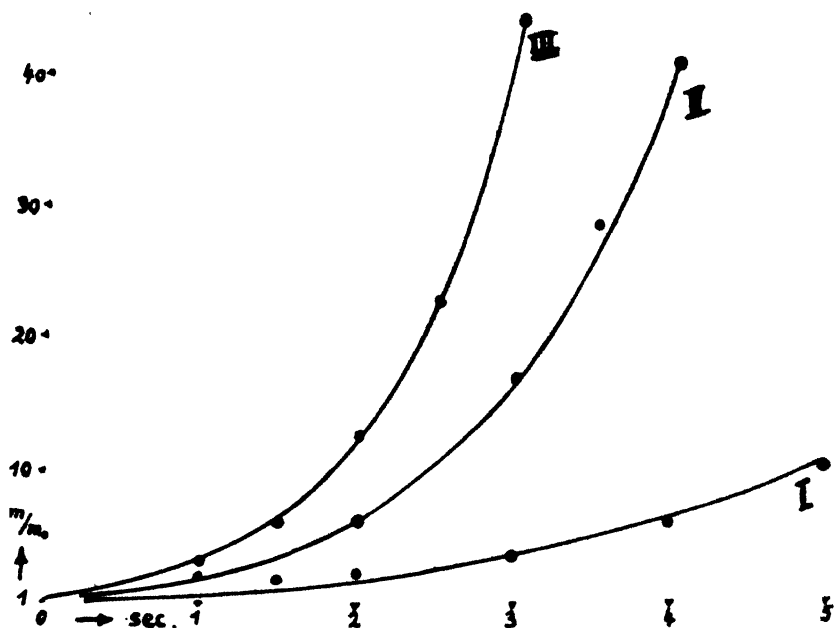


FIG. 9.

constant a simple relation is obtained. For constant mass-concentration c one gets:

$$c = 4 \cdot \pi \cdot r^2 \cdot d \cdot n / 3 \quad (2)$$

From eq. (1) and (2) one obtains: $E = \text{const.}/r$ or

$$E_1/E_2 = r_2/r_1 \quad (3)$$

This means that the extinction of light is inversely proportional to the average radius of the particles. Since this relation is only valid so long as the mass-concentration of the system remains constant, only very low intensities of the sound field could be used. Fig. 9 shows some results of measurements made with an aerosol consisting of paraffin oil particles suspended in air. The ordinates give the ratio of the increased to the initial mass and the abscissae the duration of the influence of the sound field. The different curves represent different sound intensities. In curve I, the amplitude of the vibrator rod was 9×10^{-3} mm., in curve II. 27×10^{-3} mm. and in curve III. 36×10^{-3} mm.

⁶ G. Mie, *Ann. Physik*, 1908, **25**, 377.

⁷ O. Werner, *ibid.*, 1923, **70**, 487.

The optical method yielded results in good qualitative agreement with the results of measuring the velocity of the falling particles.

Coagulation in Flowing Aerosols.

The rapidity of the acoustical precipitation permitted the study of the process in flowing aerosols. As the rate of coagulation increases with the sound intensity it was necessary to use sonic waves of high intensity. Experiments with powerful magnetostriction-generators using longitudinally divided tubes to which end-pieces of large area were affixed gave very satisfactory results. The extremely simple and efficient source of intense sound waves we have used was the air-jet generator described by Jul. Hartmann,⁶ in which a high pressure air-jet is employed which has a velocity greater than that of sound. Along such an air-jet a periodicity of pressure can be observed. If the mouth of a cylindrical pipe is brought to a place where the Pitot-pressure is increasing, very powerful sound waves will be generated in the cylinder, the frequency of which depends, of course, upon the dimensions of the cylindrical resonator. Fig. 10 shows the air-jet generator built into a simple apparatus which has also proved to be convenient for lecture experiments.⁷ To two sides of the

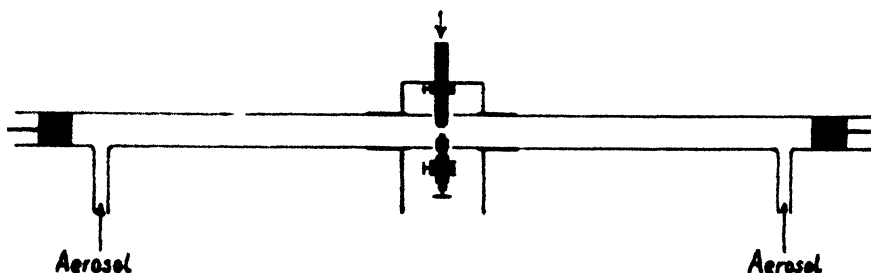


FIG. 10. —Air-jet generator.

generator are affixed tubes (1 metre long and 30 mm. in diameter) which can be tuned by pistons at the opposite ends so that stationary waves will be produced. The aerosol to be studied enters the sounding tubes by means of inlets near the pistons and then flows towards the generator. If the generator is working nearly all the suspended particles will coagulate and be precipitated at the bottom of the tubes. With this simple apparatus somewhat large amounts of aerosols could very efficiently be precipitated: e.g., 200 litres per minute of highly concentrated aerosols such as tobacco smoke or NH_4Cl particles suspended in air. The efficiency of the precipitation was measured by nephelometric methods. Comprehensive studies on the precipitation of many aerosols of a very different nature have been made; these will shortly be reported elsewhere. Every true aerosol may be coagulated and precipitated in the above manner.

The Shape of the Aggregated Particles.

The above-mentioned evaluation of the velocity of the falling particles and of the extinction of light was based on the assumption that the particles are spherical. For liquid particles this assumption may safely be made. We thought it interesting to study the appearance of acoustically aggregated dry particles such as NH_4Cl and tobacco smoke. Fig. 11 is a photomicrograph of coagulated tobacco smoke. The particles clustered in the gas space have settled down on a cover-glass. The

⁶ Jul. Hartmann, *Physic. Rev.*, 1922, 20, 719; *Phil. Mag.*, 1931, 11, 920.
Jul. Hartmann and B. Trolle, *J. Scient. Instr.*, 1927, 4, 101.

⁷ The apparatus was first used in a lecture experiment by E. Hiedemann in the *Haus der Technik* in Essen on the 13th November, 1935.

precipitated particles resemble a very viscous medium in which granular particles are embedded. The drop-like aspect of the smaller particles suggests that their shape in the gas space does not materially differ from the spherical. As has been shown by earlier investigators (see *e.g.*, Whytlaw-Grey and Patterson) one has to expect in dust a non-spherical structure. The high degree of aggregation produced in the sound field leads to a very flocculent structure of the clusters. Fig. 12 is a photomicrograph of NH_4Cl clusters formed by the sound field. The structure is evidently chain-like. Fig. 13 is a photomicrograph of suspended NH_4Cl particles made before the generator was connected. Figs. 12 and 13 illustrate convincingly the extent of the increase in size produced in the sound field. The production of highly aggregated particles by our acoustical method is very rapidly brought about. The application of this method to a comprehensive study of the structure of aggregated particles might perhaps be convenient.

Theoretical Discussion.

The effect of a sound field on suspended particles was first studied by W. König.¹⁰ The work of König was continued with great success by Andrade.⁴ S. W. Gorbatschew and A. B. Severny¹¹ have recently sought to discuss the forces in a sound field which may produce an aggregation of the suspended particles.

A comprehensive theoretical discussion of the process will be given shortly by the authors in another paper. Their theoretical calculations are partly based on the results of König and Andrade and partly on new considerations.¹² It will only be briefly outlined here.

For particles oscillating in a stationary wave the elongation x_{mom} is given by :

$$x_{\text{mom}} = A \sin \frac{2\pi a}{\lambda} \cdot \sin \omega t \quad . \quad . \quad . \quad (4)$$

where a represents the distance of the particle from the node, λ the wave-length of the sound waves, $\omega/2\pi = n$ the frequency of the oscillations, and A the amplitude of the particles at the antinode.

The difference between the velocity of the gas particles and the suspended particles, is not great so long as the particles take part in the oscillation. The Stokes' formula may therefore be used to calculate the force operating at any moment on a particle :

$$K = 6\pi r \cdot \eta \cdot \Delta v \quad . \quad . \quad . \quad (5)$$

where η represents the coefficient of viscosity of the gas, r the radius of the suspended particle, and Δv the difference between the velocity of a suspended particle and that of a particle of the gas. From equations (4) and (5) one gets the differential equation :

$$m \cdot \ddot{x} = 6\pi r \eta \left(A \cdot \omega \sin \frac{2\pi \cdot a}{\lambda} \cdot \cos \omega t - \dot{x} \right) \quad . \quad . \quad . \quad (6)$$

The solution of this equation for the stationary case is given by

$$x = \frac{A \cdot \sin \frac{2\pi a}{\lambda} \cdot \sin (\omega t - \phi)}{\sqrt{\left(\frac{4\pi d \cdot r^2 \cdot n}{9\eta} \right)^2 + 1}} \quad . \quad . \quad . \quad (7)$$

¹⁰ W. König, *Ann. Physik*, 1891, **42**, 353 and 349; **43**, 43; *Z. physik. chem. Unterr.*, 1895, **8**, 193.

¹¹ S. W. Gorbatschew and A. B. Severny, *Kolloid. Z.*, 1935, **73**, 146.

¹² O. Brandt and H. Freund, *Z. Physik*, 1935, **94**, 352, see footnote.

in which d is the density of the particles. The ratio of the amplitude X of the suspended particle to the amplitude G of a particle of the gas is given by :

$$\frac{X}{G} = \frac{1}{\sqrt{\left(\frac{4\pi d r^2 \cdot n}{9 \cdot \eta}\right)^2 + 1}} \quad (8)$$

Equation (8) may also be easily derived from the well-known formula given by König¹⁰ by simplifying some expressions in that formula. The simple equation (8) is no less valid than the formula of König but it is much more convenient to handle. It is at once seen from equation (8) that for constant values of d and η the ratio X/G of the amplitudes is determined by the value of $r^2 \cdot n$. If the ratio X/G has a definite value the product $r^2 \cdot n$ has also a definite value which may be calculated by equation (8). In other words a given ratio X/G and a given radius of the particles always correspond with a definite frequency n . The product $r^2 \cdot n$ is therefore a critical relation with regard to the behaviour of the particle in the sound field.

In view of the aniso-dispersity of the aerosol it follows from this critical relation that (for the various suspended particles of the size usually present in aerosols) there always will be found a frequency between 5 and 50 k.c., where suspended particles of different sizes will also have different amplitudes. The difference will become greatest if part of the particles has already been increased by aggregation.

The differences in the amplitudes of the oscillating suspended particles occurring at these frequencies due to the aniso-dispersity of the system may cause the oscillating particles to collide in another and far more efficient way than that considered by Gorbatschew and Severny, who did not take into account the importance of the aniso-dispersity. Calculation of the efficiency of this effect shows that an appreciable amount of aggregation, due solely to these collisions, will occur only at high stages of concentration. Not only are the direct collisions of the particles efficient, however, but even the approach of the particles to one another is of importance, since it increases the probability of aggregation due to other effects. Quantitative calculations of the effect due to this approach of the particles are not yet possible.

The hydrodynamical forces of attraction as considered already by König must also be taken into account. It appears that importance must be attached to the observations of Andrade on vortex formation among particles which do not or only partially take part in the oscillation. Quantitative calculations as to the efficiency of vortex formation have also not yet been made.

The effect of the forces of attraction connected with the pulsation of spheres (studied by Bjerkness) has been considered in the paper of Gorbatschew and Severny. This effect is evidently of less importance with regard to the process of rapid coagulation since dry aerosols, in which no pulsation or a virtual pulsation will take place, may also be precipitated.

High Frequencies.

The above-mentioned experiments were made with frequencies between 5 and 50 k.c., mainly between 10 and 20 k.c. At frequencies of some hundreds of kilocycles precipitation of smoke can also be observed

as was first reported by E. B. Pearson.¹⁸ The phenomena occurring at the high ultrasonic frequencies cannot be directly compared with those at the frequencies of rapid coagulation. One essential difference is the fact that at these high frequencies not all the particles oscillate; under certain conditions no coagulation occurs at all. Several particles rotate around another without colliding. Fig. 14 shows the experimental arrangement. *Q* is the piezo-electric crystal, *R* is the horizontal sounding tube, and *M* the microscope. If the microscope is focussed on a layer just above the bottom of the tube the rotating particles can be readily observed as they do not disappear from the range of vision by sedimentation, but move only in a horizontal direction towards the nodes. They appear to be kept at this distance from the bottom by vortices (they disappear at once on disconnecting the ultrasonic generator). The

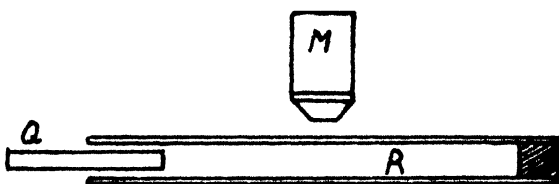


FIG. 14.—Ultrasonic arrangement.

particles moving to the nodes settle down there; these particles are very small compared with those formed by the process of rapid coagulation. Because of these and other effects the problem of aggregation produced by ultrasonic waves of high frequency needs still further investigation before it seems advisable to communicate any definite results.

Summary.

The process of rapid coagulation by sonic and supersonic waves at frequencies between 5 and 50 k.c. is studied. Photomicrographic and kinematographic observations prove that the process of aggregation takes place in the sound field itself, and give suggestive information about the effect of the sound on the disperse system.

The enlargement of the particles was measured by two different methods. The results show that the particles may easily increase in size more than a hundredfold under the influence of the sound field.

Flowing aerosols may very efficiently be coagulated and precipitated if sufficiently large sound intensities are used.

No complete theory of the process can yet be given, as some of the complex factors cannot yet be calculated quantitatively. It could be deduced that the aniso-dispersity of the system must be taken into account when discussing the process.

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¹⁸ E. B. Pearson, *Proc. Physic. Soc., London*, 1935, 47, 136.

THE COAGULATION OF SMOKE BY SUPERSONIC VIBRATIONS.

By E. N. DA C. ANDRADE, D.Sc., Ph.D., F.R.S.

Received 26th February, 1936.

In a paper concerning the behaviour of particles in a column of vibrating air¹ I drew attention to the fact that smoke particles in air vibrating at supersonic frequencies would behave much like smoke or other dust particles in air vibrating at sonic frequencies.² Later E. B. Pearson, working in my laboratory, carried out some experiments on the subject,³ and observed a rapid coagulation of tobacco smoke in air subjected to supersonic vibrations ranging from 92 to 801 kc./sec. He found that the coagulated particles formed double lines on the walls of the tube in the neighbourhood of the nodes, reminiscent of the heaps of dust which form to either side of the nodes in the familiar Kundt's tube experiment, and he was able to measure the velocity of sound at supersonic frequencies by means of these nodal figures. Mr. R. C. Parker, who is continuing such experiments, has obtained the phenomenon in a particularly clear manner, as illustrated in Fig. 1, which shows the rings obtained with magnesium oxide smoke at a frequency of 220 kc./sec.

It seems worth while to examine the theoretical aspect of the coagulation. Spheres at rest in a vibrating medium repel one another if their line of centres is parallel to the vibration vector, but attract one another if the line of centres is normal to this direction.⁴ The force of attraction or repulsion varies inversely as the fourth power of the distance, and directly as the square of the (maximum) velocity of the vibrating fluid. This attraction of particles suitably placed is sufficient to account in a general way for the coagulation.

The calculations which lead to the results just quoted make many assumptions. In the first place, that the particles are at rest in the fluid, which certainly does not hold with the smallest particles. For instance, at 300,000 \sim , for smoke particles, of density $\rho = 1$ and radius $r = 5 \times 10^{-5}$ cm., the ratio w_0/v_0 is 0.182, where w_0 is the velocity amplitude of the sphere and v_0 that of the surrounding air, while for smaller and lighter particles w_0/v_0 will be greater. For the purposes of obtaining an average value of the force for all particles it will, however, suffice to consider the particles as fixed if we take for the maximum velocity of the vibrating air the relative velocity $v_0 - w_0$, in place of v_0 . A more serious point is that the calculations assume that the motion of the air surrounding the spheres is vortex-free, whereas under certain conditions, which ordinarily prevail in, for instance, a Kundt's tube, each particle is surrounded by a vortex system which governs the forces between the

¹ *Proc. Roy. Soc.*, 1931, 131A, 445, referred to in the present paper as "Circulations."

² See in this connection an interesting letter by H. S. Patterson and W. Cawood, *Nature*, 1931, 127, 667.

³ *Proc. Physic. Soc.*, 1935, 47, 136.

⁴ Walter Koenig, *Ann. Physik*, 1891, 42, 353 and 349, and 1891, 43, 43. Also E. N. da C. Andrade, *Phil. Tran. Roy. Soc.*, 1932, 230A, 413.

particles.⁵ The general explanation of the coagulation is not vitiated even if vortex systems are found, for two particles with transverse lines of centres are still attracted, but the law of force has not been worked out in the case of vortex motion, so that, if it takes place, no attempt at a quantitative theory can be made.

Let us first examine if the assumptions of vortex-free motion can be supported in the case of ordinary smokes. It has been shown⁶ that for small spheres the conditions which govern the initiation of vortex motion are expressed by

$$\frac{nad}{\nu} > 4.6$$

where $n = 2\pi f$, f being the frequency of the vibration: d is the diameter of the sphere: a the amplitude of the air vibration: ν the kinematic viscosity of the medium. The smallest spheres for which this law was proved were 0.25 mm. in diameter, and the greatest value of n was 7540, so that in extending it to the supersonic case we are extrapolating beyond our experimental range. There are, however, theoretical reasons for

supposing that this extension is justified. The value of $\frac{1}{d}\sqrt{2\nu/n}$, is not very different in the experiments in question and in the supersonic case, and it is apparently only large differences in this quantity, and then in a direction other than that which holds in the present case, that render the extrapolation invalid.⁷

If $f = 100$ kc./sec. and the value of ν be taken as 0.15 (air), then formula (1) gives $ad > 1.1 \times 10^{-6}$: if $f = 800$ kc./sec., $ad > 1.3 \times 10^{-7}$.

If therefore $d < \frac{1.3 \times 10^{-7}}{a}$ we need not anticipate vortex motion even at 800 kc./sec., while even for $d < \frac{1.1 \times 10^{-6}}{a}$ we are safe at 100 kc./sec.

We can make a rough estimate of the greatest value of a from the breaking strength of quartz crystals. Taking this as 9×10^{10} dyne/cm. (given as maximum value in *International Critical Tables*, 4, 22) we get for the maximum velocity at the crystal face 700 cm./sec., which at $f = 800$ kc./sec. gives an amplitude of 1.4×10^{-4} cm., and at $f = 100$ kc./sec. gives 1.1×10^{-3} cm. Owing to resonance these values will be exceeded in the air column, but against this the crystal is never run near amplitudes that lead to fracture normal to the axis. If we take these figures as giving roughly the amplitude of the air vibration, we see that we shall not get vortex motion unless $d > 10^{-3}$ cm. Another factor that will tend to suppress vortex motion with smaller particles is that as the particles get smaller the *relative* velocity of air and particle decreases.

We are justified, then, in assuming vortex-free motion. In this case the force between two spheres each of radius r , at distance d from one another, is given by

$$\left. \begin{aligned} X &= -\frac{3}{2} \frac{\pi \rho r^6 \omega_0^2}{d^4} \sin \theta (1 - 5 \cos^2 \theta) \\ Y &= 0 \\ Z &= -\frac{3}{2} \frac{\pi \rho r^6 \omega_0^2}{d^4} \cos \theta (3 - 5 \cos^2 \theta) \end{aligned} \right\} \quad . \quad . \quad (1)$$

⁵ *Circulations*, p. 454, et seq.

⁶ *Ibid.*, p. 463 et seq.

⁷ *Ibid.*, p. 467.

where θ is the angle which the line of centres makes with the direction of the vibration velocity W . The force is thus proportional to $\frac{r^6 w_0^2}{d^4}$.

The repulsion which takes place when the line of centres of the particles approaches the direction of the vibration vector need not concern us, as the only effect which it can have on coagulation is a secondary one.

Two particles of the size contemplated, moving together under an attractive force of the magnitude in question, can, in a viscous medium such as air, be supposed to move at a speed proportional to the force and inversely as the surface. The assumption that the resistance is proportional to r^2 is, of course, a provisional one, as the problem of a sphere moving through a liquid oscillating at right angles to the motion has not been solved, to my knowledge. For a sphere simply oscillating in a viscous liquid, however, the component of the resistance which assumes importance for our frequencies and linear dimensions ($n = 2 \times 200$ kc. per sec., $a = 10^{-4}$ to 10^{-5} cm.) is proportional to r^2 . The oscillations in our case are, of course, transverse to the travel. The consideration of the accelerated motion of a sphere through the liquid is very complicated, involving as it does $\frac{dv}{dt}$ and terms in r^3 , r^2 and r . The selection here made of r^2 is justified by the fact that measurements by Mr. Parker, carried out after the calculation had been completed on this basis, agree very well with the formula deduced.

On this assumption the time taken for the particles, of fixed radius r , to move from a distance d until they are in contact, at distance $2r$ between centres, is

$$t = K' \int_{2r}^d x^4 dx = K(d^5 - 32r^5)$$

K is a constant during the movement of the particles up to the time when they touch and adhere, but is inversely proportional to $r^4 w_0^2$. Let M = mass of smoke per c.c., whatever the concentration, so that we are dealing with the coagulation before an appreciable amount of smoke has settled, and N the number of particles at any moment.

$$\text{Then mass of single particles} = \frac{M}{N} = \frac{4}{3} \pi r^3 \rho$$

$$\therefore r = AN^{-\frac{1}{3}}$$

$$\text{where} \quad A = \left(\frac{3M}{4\pi\rho} \right)^{\frac{1}{3}} \quad (2)$$

The average distance between the particles = $d = N^{-\frac{1}{3}}$. The relative velocity of air and particle, in the case where the particles are not so heavy as to remain fixed while the air washes over them, is

$$v = \left(\frac{1 - w_0}{v_0} \right) v_0$$

where w_0 is the maximum velocity of the particle during vibration, and v_0 that of the air.

Hence τ = time in which number N of particles is halved,

$$\begin{aligned} &= BN^{\frac{1}{2}} \frac{1}{v_0^2} \left(1 - \frac{w_0}{v_0}\right)^{-2} (N^{\frac{1}{2}} - 32A^{\frac{1}{2}}N^{-\frac{1}{2}}) \\ &= BN^{\frac{1}{2}} \frac{1}{v_0^2} \frac{1}{\left(1 - \frac{w_0}{v_0}\right)^2} (1 - 32A^{\frac{1}{2}}) \\ &= PN^{-\frac{1}{2}} \left(1 - \frac{w_0}{v_0}\right)^{-2} \quad \dots \dots \dots (3) \end{aligned}$$

where P is constant for a given mass of smoke and velocity-amplitude of the air.

Let us suppose that, at the frequency concerned, even the smallest particles with which we deal are not appreciably entrained, *i.e.*, w_0/v_0 is negligible. Then, considering the process as a continuous one

$$- \frac{dN}{N} = C'N^{-\frac{1}{2}} dt$$

or

$$\begin{aligned} dt &= -C'N^{-\frac{1}{2}} dN \\ t &= C(N_0^{\frac{1}{2}} - N^{\frac{1}{2}}) \quad \dots \dots \dots (4) \end{aligned}$$

which gives an initially rapid falling off of number of particles with time, becoming slower as time increases. Fig. 1 represents this law.

Formula (4) gives a coagulation rate which is independent of frequency, because w_0/v_0 has been taken as zero (particles at rest in oscillating medium). Actually, however, w_0/v_0 while exceedingly small for very high frequencies, approaches unity as the frequency diminishes, and it is this that makes rate of coagulation increase with frequency. The factor w_0/v_0 is also a function of the particle size, decreasing as the particle size increases, so that for lower frequencies, where w_0/v_0 is initially not negligible, the curve of Fig. 1 gives a rate of coagulation that is too rapid in the initial stages as compared with the later stages. The quantitative relation is given by the somewhat complicated formula *

$$\frac{w_0}{v_0} = \frac{\{1 + 3b + 9/2b^2 + 9/2b^3 + 9/4b^4\}^{\frac{1}{2}}}{\{a^2 + 3ab + 9/2b^2 + 9/2b^3 + 9/4b^4\}^{\frac{1}{2}}} \quad \dots \dots \dots (5)$$

Here $a = \frac{2\sigma + 1}{3}$, where σ is the ratio of the density of the particles to

that of the medium, while $b = \frac{1}{r} \sqrt{\frac{\nu}{\pi n}}$. For instance with particles of magnesium oxide ($\rho \doteq 0.35$) in air, $a = 200$; with tobacco smoke $a = 820$. With air

$$b = 0.087 \frac{1}{rf^{\frac{1}{2}}} = \frac{0.087}{A} \frac{N^{\frac{1}{2}}}{f^{\frac{1}{2}}} = B \frac{N^{\frac{1}{2}}}{f^{\frac{1}{2}}} \quad \dots \dots \dots (6)$$

In any particular case, therefore, we can find the value of B , and, substituting in (5), obtain w_0/v_0 as a determined function of N and f . If we substitute this in (3) we have a relation between τ and N which involves f and known constants only.

Equation (5) can be simplified only in certain cases, which are best considered as they arise, that is, when particular experiments, with known

* W. König, *Ann. Physik*, 1891, 42, 353. See also E. N. da C. Andrade, *Proc. Roy. Soc.*, 1935, 134A, 445.

values of B , are in question. It may, however, be pointed out that if $M = 3 \times 10^{-7}$ gm./cm.³, which gives, from (2) and (6), $B = 14.8$ with $\rho = 0.35$: $r = 5 \times 10^{-5}$ cm. initially: $f = 300,000$: then, in (6), $b = 3.2$, and we can neglect $9/2 b^2 + 9/4 b^3 + 9/4 b^4$ in comparison with $a^2 + 3ab$, as amounting to about 1 per cent., and decreasing as coagulation takes place. We can then use the simplified expression

$$\left(1 - \frac{w_0}{v_0}\right)^2 = \frac{\{(a^2 + 3ab)^{\frac{1}{2}} - \frac{3}{2}b(2b + b^2)^{\frac{1}{2}}\}^2}{a^2 + 3ab}.$$

In general, however, further simplification is not possible, owing to the values of b being neither small nor great compared to 1.

As an example we may take the following figures, where $(w_0/v_0)_0$, $(w_0/v_0)_{.5}$, and $(w_0/v_0)_{.1}$, represent the initial value and the values after the number of particles has been reduced to one-half and one-tenth respectively. The initial radius r is taken as 5×10^{-5} cm.

f .	$(w_0/v_0)_0$.	$(w_0/v_0)_{.5}$.	$(w_0/v_0)_{.1}$.
300,000	0.01	negligibly small	
75,000	0.111	0.050	0.008

This shows that at $f = 300,000$, Fig. 1 should represent the state of affairs without correction. At $f = 75,000$ the initial rate is

$$(1 - w_0/v_0)^2 = 0.79 \text{ times,}$$

and the rate after N has been reduced to a half is 0.90 times, the value given by Fig. 1, the rates for values of N less than $0.1 N_0$ being appreciably the same.

Since this paper was first communicated to the Society Mr. Parker has carried out experiments which have confirmed formula (4), and so substantiated the general correctness of the theory.

EXPERIMENTS ON COAGULATION BY SUPER-SONIC VIBRATIONS.

BY R. C. PARKER, B.Sc.

Received 7th April, 1936.

Professor E. N. da C. Andrade suggested to me that I should look into the question of the coagulation of smoke by supersonic vibration experimentally, with the object of seeing how far the formula which he has derived actually represents the variation of the number of particles with time. The experiment has been carried out with magnesium oxide smoke in air, vibrating at a frequency of 220 kc./sec. In the method used the vibration is allowed to continue for a given time, and the concentration is then determined. The natural coagulation during the period of measurement is negligible, and it has been found possible to reproduce a standard initial concentration with great consistency.

The particle concentration was determined in a manner similar to that employed by Perrin for counting particles in a dilute colloidal solution in his experiments on Brownian motion. The freely suspended particles were viewed through an ultramicroscope fitted with a Zeiss 23.5 mm. achromatic objective, the number visible being that contained in a volume equal to the product of a prescribed area of the field of view and the depth of focus

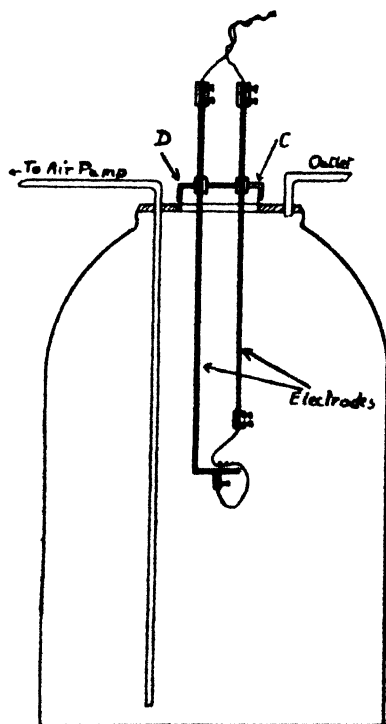


FIG. 1.

rotation. It was found necessary to eliminate any motion of the particles that might arise from convection, otherwise the number of particles seen in the field of view would depend upon their velocity. The several precautions adopted to minimise this source of error are detailed in a forthcoming paper by Andrade and Parker; they are chiefly concerned with the method of insulating the tube against any local temperature variations, and ensuring that its temperature is that of the entering smoke-laden air.

The magnesium oxide smoke was obtained by burning 9.7 mgm. of magnesium ribbon in a stone jar of 12 cubic litres capacity. A diagram of the arrangement used is shown in Fig. 1. A brass cap C, which served to support two long electrodes, fitted closely over an opening in a metallic plate, cemented so as to close the jar. To the lower electrode was fixed an asbestos covered cup on which was placed the requisite amount of magnesium ribbon. Connected across the electrodes, and in close contact with the magnesium ribbon, was a length of resistance wire. The mag-

field of view to be restricted within known limits, according to the type of graticule used and the number of squares considered. The concentration was then ascertained by noting the number of particles which could be seen instantaneously in a known volume. A photographic shutter, placed in the path of the illuminating beam, was opened every two seconds for the duration of half a second, and the number of particles noted at each exposure. This number never exceeded 7 or 8. The final values given below (Table II.) represent, for each concentration, the mean of about 720 counts and have a probable error of less than 1 per cent. Only 120 counts were made for any one given filling, after which time the contents of the tube were renewed and the air was set into vibration for the requisite period. Owing to the steady condition of the smoke any local irregularities in its distribution tended to persist over several counts, and hence a more representative value was obtained by selecting for observation each graticule square in

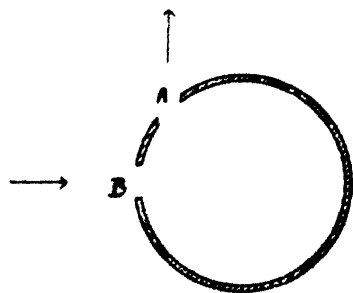


FIG. 2.

netic ribbon was a length of resistance wire. The mag-

nesium ribbon was ignited by passing a current through the resistance wire, and filled the jar with smoke. To determine whether this process gave reproducible results it was repeated six times, the initial smoke concentration being each time ascertained by counting. The values obtained

TABLE I.

Details of count for one determination of the initial concentration. There were six separate fillings, and three sets of 40 counts were made for each filling.

For fillings 1, 3 and 5 counts were made by observer A.

Filling	1.	2.	3.	4.	5.	6.
Number of particles counted	108	92	109	101	88	101
" " " "	86	95	102	110	91	82
" " " "	81	101	107	82	77	94
Total	275	288	318	293	256	277
Total number observed by A					849	
" " " " B					858	
Mean number per unit volume					23.7	

by two observers making 360 counts, are detailed in Table I., and, as may be seen, their mean values obtained by the two observers agree to within 1 per cent. To make certain that, in the absence of a sound field, the normal coagulation and settling under gravity was small, observations were extended over eight minutes, there being exhibited, during this time, no fall in the concentration.

The smoke, on which the above observations were made, was contained in a glass tube of length 10.5 cm and internal diameter 2 cm. One end of the tube was closed by a flat glass disc, while the other end was closed by a cylindrical quartz crystal oscillator which fitted with a small clearance all round. Fig. 2 is a cross-section through the tube at the point, 6 cm. from the oscillator, where the observations were made. The holes A and B were closed by windows of very thin

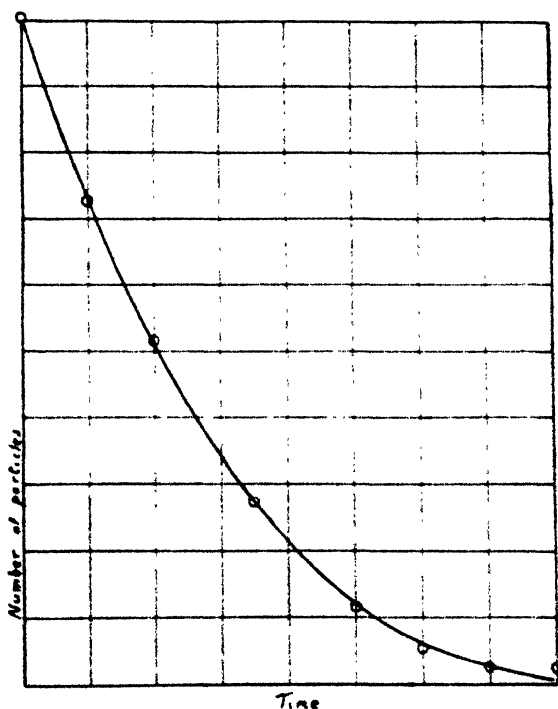


FIG. 3.

glass (the iridescent fragments of a quickly blown bulb) smoothly stuck to the inner surface of the tube, care being taken to avoid any projection which might cause vortex motion. A pointolite lamp, in conjunction with

a convenient optical system, was employed to illuminate the field of view, and a water cell, 12 inches long, containing a solution of cuprous ammonium sulphate eliminated any heating effect which the beam might have.

The values for the particle concentration were obtained for 8 values of t , the time during which the supersonic vibrations were maintained. The greatest value of t was eight minutes, which caused the number of particles to fall to about 1/40th of the initial value. The eyepiece graticule chosen for the lowest concentration gave an area of observation 16 times

TABLE II.

Time t (Minutes).	No. of Particles per Unit Volume (Each Determination Representing the Mean of 120 Counts).		Mean Value.	Corresponding Values used as Ordinates in Fig. 3.
	Observer A	Observer B		
0	22.9 20.5 21.3	24.0 24.4 23.1	23.7	10.0
1	17.1 19.0 14.9 16.2	18.0 15.0 18.0 18.5	16.8	7.28
2	12.6 11.1 12.0	12.5 10.6 14.0	12.1	5.16
3½	6.50 6.64	6.20 6.56	6.47	2.74
5	2.70 2.20	2.90 3.20 2.90	2.78	1.18
6	1.25 1.26	1.45 1.22 1.16 1.50	1.31	0.56
7	0.69 0.62	0.64 0.54 0.63 0.60	0.62	0.26
8	0.60 0.58	0.68 0.57 0.71	0.63	0.27

that used at the highest concentration. Unit volume was taken as that bounded by the graticule square of smallest area, as used in determining the initial concentration. At the very low concentrations, i.e., when the time interval was six to eight minutes, there was a tendency to include certain small non-coagulated particles which were present, and were more obvious when, as occasionally happened, there were no coagulated particles in the field of view. The observations were divided between two observers, whose estimates were in good agreement. As there was usually a number of particles visible, that were not in focus, a certain amount of practice was found necessary: then, ultimately, very satisfactory consistency was obtained.

Table II. gives the values obtained for various times of the coagulating vibration, each value in the fourth column being the mean of about 700 counts. In Fig. 3 is drawn the theoretical relation between the concentration and time, the points plotted being those experimentally determined. The resulting agreement is, as may be seen, extremely close, and there can be little doubt that the mechanism considered in the theoretical treatment closely corresponds to the existing conditions. Too much reliance must not be placed upon the slight deviation shown at low concentrations, for it is there that the experimental observations become less consistent.

GENERAL DISCUSSION.*

Dr. E. G. Richardson (*Newcastle*) said: The authors have established that there is a range of frequency in the supersonic region most effective for coagulation; is there not also a most effective amplitude range? Mr. T. Laidler and I, at Newcastle, measuring the velocity of sound in aerosols, found that coagulation may be to a large extent inhibited, even when using a supersonic source, if the amplitude is kept to a minimum. On the other hand, a large amplitude is known to favour dispersion, as in the production of emulsions by supersonics.

Brandt and Hiedemann have used optical absorption to measure the change of particle size during coagulation, citing the work of Wiener as justification for the assumption that the absorption of light is proportional to the square of the particle diameter. Though this method is very precise, yet I think the results they have obtained from it require correction. Wiener was concerned with transparent particles, i.e., fogs. I have verified the same law for the extinction of light by opaque particles in suspension down to 10μ , yet for diameters between 10μ and 1μ Cheveneau and Audubert¹ have shown that an extinction coefficient proportional to the diameter fits the results better. What was the range of particle size in the present experiments?

Mr. G. W. Slack (*Leeds*) said: it may be questioned whether any differentiation, in the later stages of coagulation, between coagulated and uncoagulated particles is desirable in what is fundamentally a statistical investigation, since any such distinction must obviously be made on an arbitrary size-basis and since, moreover, it is impossible to say at what time this process should be started. If we count *only coagulated particles* then the number at the start must be taken as zero, whilst on the other hand if we count *all* the particles, then, towards the end, Mr. Parker's counts are admittedly too low and the divergence from the theoretical expression of Professor Andrade will be in the same direction as the results of Brandt and Hiedemann,² and also in accordance with the qualitative experiments of Patterson and Cawood³ who found a distinct tendency for small particles to persist after the major portion had flocculated out.

From the paper it is not clear that the smoke must have been diluted, or otherwise treated in some way, to reduce the number of particles, since on making a cloud of the mass concentration given the numbers fell rapidly from 5×10^7 to 5×10^6 in $0\frac{1}{2}$ mins.

Dr. K. Söllner (*London*) said: Liquid, non-metallic substances are dispersed into gases by the same mechanism as that which causes emulsification in liquid/liquid systems, i.e. cavitation, as was shown a short time ago.⁴ When the sound travels through the liquid, the latter is stretched locally and disrupts there, forming a cavity. If an external force (e.g. gas pressure) acts from outside this cavity collapses vehemently, as was shown by Lord Rayleigh.

* On the three previous papers

¹ *Ann. Physique*, 1920, 13, 133

² *This vol.* (Table II. and Fig. 9).

³ *Smoke*, Whytlaw-Gray and Patterson, p. 183.

⁴ C. Bondy and K. Söllner, *Trans. Faraday Soc.*, 1935, 31, 835.

Attention should be drawn also to the papers on orthokinetic coagulation by G. Wiegner and co-workers, chiefly Tuorila,⁶ who have developed a theory, which takes into account the different velocities of particles of different size, when an external force acts upon the whole system, e.g. the different rate of sedimentation in a suspension of particles of different size causes collisions between these particles, thus increasing the rate of coagulation. This orthokinetic coagulation was very helpful in understanding the coagulation of emulsions by ultrasonics,⁶ and it may be applied profitably also to gaseous systems.

Mr. A. G. Grant (*Darlington*) said: These very interesting papers on particle coagulation by sonic and supersonic means, open up a wide field of speculation. At the present time there are many simple means of removing coarser particles from gases, and it is the fine particles which introduce complexity and expense. I wonder if sonic coagulation will prove capable of large scale application as a preliminary to electrical precipitation or other known means of particle extraction.

Dr. R. Lessing (*London*) said that Mr. Grant's suggestion that the primary aggregation of particles by supersonic waves might form a first step in the industrial elimination of dispersoids from gases, had an analogue in the addition of flocculating agents to suspensions, which had in recent years been introduced into sedimentation and clarification practice.

Professor R. Whytlaw-Gray (*Leeds*) said: Has Dr. Hiedemann any evidence on the electrical state of the particles during supersonic coagulation? They may possibly become electrified. Has anything suggesting this been observed?

The photographs in Dr. Hiedemann's paper of the aggregates precipitated by this process exhibit the same structures on a larger scale as those formed in the much slower process of natural coagulation.

Dr. E. Hiedemann (*Köln*) said: We do not agree with Andrade when he attributes the cause of acoustic coagulation only to the forces between spheres in an oscillating medium, as comprehensively studied by Bjerkness.⁷ A direct comparison of our results and those obtained by Andrade cannot be made, as the experimental conditions were very different. At the high frequencies he used, the suspended particles do not, in effect, oscillate, whereas at the lower frequencies most of the as yet unaggregated particles oscillate. The conditions at the lower frequencies are much more complicated, as we have seen from our theoretical calculations and our experimental results. The order of magnitude of the effect of the sound field is also quite different. The process of supersonic precipitation studied by Andrade and co-workers takes some minutes to complete, whereas the rapid coagulation by sonic and supersonic waves studied in our experiments needs only a few seconds or less. I will therefore only point out some theoretical points with regard to Andrade's interesting theory. His equation (1) was derived by W. König,⁸ who used simplifying assumptions. It is difficult to judge whether these simplifying assumptions are justifiable at the very high frequencies he used, especially where the particle size is so small that molecular discontinuity cannot be neglected for precise quantitative calculations. To approach a solution of the problem it is, of course, justifiable to start with such simplifying assumptions; for this reason we have also used König's formula in calculating⁹ the order of magnitude of the Bjerkness' forces of attraction in the process of coagulation. We preferred to assume the force of the resistance of the medium to the approaching particles to be proportional to r , whereas Andrade has chosen r^2 . The law of resistance

⁶ Cf., e.g., G. Wiegner, *J. Soc. Chem. Indust.*, 1931, **50**, 55; P. Tuorila, *Kolloidchem. Beihfte*, 1927, **24**, 1, 27.

⁷ K. Sollner and C. Bondy, *Trans. Faraday Soc.*, 1936, **32**, 616.

⁸ W. Bjerkness, *Vorlesungen über hydrodynamische Fernkräfte nach C. A. Bjerkness Theorie*, Bd. 2, 1900-02.

⁹ W. König, *Ann. Physik*, 1891, **42**, 353 and 549; **43**, 43.

¹⁰ O. Brandt, *Dissert.*, Köln., Feb., 1936.

for particles moving at right angles to the oscillation of the medium is as yet unknown, but if one assumes that the motion of particles towards one another is independent of the oscillation of the medium at right angles to that motion, the resistance must be assumed to be proportional to r until somewhat large particle velocities are obtained. If one considers particles of diameter 1μ , Reynolds' number is smaller than 0.2, so long as the velocity of the particles is smaller than 600 cm./sec.

The anisodispersity of the system is another serious difficulty, especially as we have seen from our measurements that incipient aggregation has the effect of rendering the system still more anisodisperse. One would also conclude from Andrade's equation (1) that the largest particles coagulate first as the forces of attraction are proportional to r^6 , and this would also have the result of making the system more anisodisperse.

In consequence of the large increase in mass of the particles, one would expect an accelerated sedimentation, *e.g.* similar to that shown in Fig. 1 of the paper. Could the mass-concentration M in equation (2) be made constant?

Notwithstanding these difficulties, the agreement between Andrade's and Parker's experiments is excellent. But even this cannot suppress another serious doubt. The calculations are made for particles of a strictly spherical shape, but the experiments were made with magnesium oxide smoke. Even if one could assume the primary particles to have an approximately spherical shape, one must consider that after the first aggregation of two particles the enlarged particles are not spherical at all; for increased coagulation the structure will be very flocculent.

Although one approaches with diffidence the simplifying assumptions of Andrade's theory, the agreement between the theory and the experimental results is so remarkable that one may hope to obtain reliable knowledge of the forces causing aggregation at high supersonic frequencies.

Mr. R. C. Parker (*London*) in reply, said: The distinction made between the coagulated and uncoagulated particles did not play the important part in the observations which Mr. Slack suggests. A few small non-coagulated particles were observed at all stages, and were clearly very different in size, as judged by their brightness, from the main body of particles. After 6 or 8 minutes, when the coagulated particles were very scarce, the smaller particles were comparable in number with the now very much larger particles which were counted. From the point of view of the problem under consideration the uncoagulated particles should clearly not be taken into account. What is in question is not the number of particles, but the number of effective unions, a large number of which go to the making of one larger particle. That the distinction made was not an arbitrary one is clearly shown by the fact that two independent observers, working without any possibility of conscious or unconscious collusion, obtained consistent results.

Mr. Slack has, later, confounded the concentration in the stone jar, in which the smoke was originally produced, with that existing in the observation chamber. The smoke produced in the stone jar was highly concentrated and coagulated rapidly, as would be expected from the work of Whytlaw-Grey and his collaborators. After standing for some minutes, however, the smoke was passed through several pipes and a calcium chloride drying tube, where further coagulation and filtration took place. The result was that the smoke, as initially observed in the observation chamber, had a concentration of 10^8 particles per cm.³, which did not diminish appreciably in the time concerned. Extremely slow coagulation at this concentration would be anticipated from the work of the Leeds school.

Professor E. N. da C. Andrade (*London*), in reply to Dr. Richardson, said: The variation of coagulation with amplitude is a point of great importance, which has not yet been investigated. According to my ideas the rate of coagulation should vary as the square of the amplitude, and measurements directed to this point would throw valuable light on the

mechanism. No experiments, however, have yet been made in this direction in my laboratory.

As regards the very interesting paper by Brandt and Hiedemann, it is to be regretted that fuller information is not given. We are not told the frequencies which were used, nor, in particular, what precautions were taken against convection, which is generally found troublesome, but which we have eventually succeeded in eliminating. Since, in Fig. 4, the sound was cut off for photographs (*g*) and (*h*), and all the streaks are in the same direction, it would appear that convection is largely responsible for the nature of the images. There seems to be no influence that could orient actual long particles all in the same direction. I am also not clear why the exposure was lengthened from $1/125$ second for Fig. 3*a*, to $1/10$ second for Fig. 3*b*. The longer exposure may play some part in the changed appearance. I am a little troubled as to why tobacco smoke particles, which are practically all water, are called dry.

The sketch of the theory is hardly full enough to justify critical consideration. I may say that, for sonic frequencies, I have found, with the assistance of Mr. R. A. Scott, that at $2300 \sim$, with an amplitude of 0.15 mm., coagulation of tobacco smoke takes place rapidly, (tube practically clear of smoke in 1 minute) whereas at $165 \sim$, and an amplitude of 1.5 mm., there was no appreciable coagulation due to the sound in half an hour, although the concentration was fairly high. If the forces which I have assumed active in my theory are really responsible for the coagulation this is easily explained, since at $2300 \sim$ there will be a small relative motion between the air and smoke particles, while at $165 \sim$ there will be practically none. With the very much greater amplitude which prevails at $2300 \sim$ than in the supersonic case, a relative motion amounting to only a small fraction of the total amplitude should be sufficient to produce marked coagulation. It is quite possible that these experiments at sonic frequencies are also explicable in general terms on the theory of Brandt and Hiedemann, since at low frequencies all particles, small and great, have about the same amplitude. I am, however, in some doubt as to how their theory can explain the results at high supersonic frequencies, where all particles, small and great, are at rest in the medium. I do not think, therefore, that the aniso-dispersity, which on their theory is responsible for the coagulation, can play any part in the supersonic case, although, of course, both it and the hydrodynamic forces may be active at sonic frequencies. Further experiment is needed on this point.

As regards the criticism of my theory, what is required to test a theory is some kind of quantitative formula which can be experimentally checked, and in the case of a problem as complicated as the present one, some kind of simplifying assumptions are necessary. Those I have made are tentative rather than well established, and I am well aware that subsequent workers may improve upon them. They do, however, furnish some indication of how the problem can be approached. As regards the resistance proportional to r^2 , the particle is not moving uniformly but rapidly accelerating, and I have given a rough reason for my adoption of this law. At any rate the application of Stokes' law is clearly not justified. I have actually tried the effect of a resistance proportional to r , and found a formula which disagrees violently with Mr. Parker's observations. This is in itself of some importance, as showing that the experimental results do not agree with practically every likely-looking formula, as might be the case.

I look forward to studying the full theory of Brandt and Hiedemann, especially in its bearing on the variation of rate of coagulation with frequency.

Dr. E. Hiedemann (Köln), said: In reply to Dr. Richardson: We have not found a most effective range; we have as yet only observed that the process of rapid coagulation is the more effective the higher the amplitudes. Although large amplitudes of supersonic waves are known to favour dispersion in liquids, such an influence on suspended systems in gases has never been reported.

Our assumption that the absorption of light is proportional to the square of the particle diameter is based upon the work of O. Werner (*loc. cit.*) W. Trabert,¹⁰ G. Mie (*loc. cit.*) and W. Findeisen.¹¹

O. Werner has measured the dependence of the absorption of light in fogs upon the particle diameter when the mass-concentration remains constant. The evaluation of his experimental curves in some cases accords with the assumption that under these conditions the extinction of light is proportional to the reciprocal particle diameter, but in other cases the agreement is not good. The different results of Chénevau and Audubert were obtained with suspended particles in liquids and may perhaps not be valid for suspended particles in gases. Most of our particles had diameters from 1.6 to 2.0 μ . During the coagulation the diameters of the particles increase rapidly to more than 10 μ . Even though our assumption should not be quite justified for the smallest particles, only the very first part of the curve would require some correction. The uncertainty of this small and as yet not important part of the curve is unavoidable as different authors cited have got different results. Another and more important uncertainty is due to the aniso-dispersity of the system. But in the evaluation of our measurements both uncertainties may safely be neglected as we only sought information upon the order of magnitude.

In reply to Dr. Söllner: In the short outline of our theory of the process of rapid coagulation we have already mentioned that we have found the anisodispersity of the system to be of importance for the aggregation.¹² The different velocity-amplitudes of the particles of different sizes bring about kinetic impacts leading to coagulation in the frequency range used.

In reply to Mr. Grant: Measurements of the energy required for the process of rapid coagulation by sonic and ultrasonic waves have so far only been made with the usual laboratory apparatus. The efficiency of the apparatus depends of course very much on the sort of acoustic generator used. With a certain generator the efficiency of the sonic aggregation could well be compared with that of electrical precipitation. But the results of experiments on a small scale do not permit definite conclusions regarding large scale application, as one knows many cases in which a chemical process, which is very satisfactory in a test-tube, is quite discouraging when tried on a large scale. It will therefore only be possible to answer this question when comprehensive experimental work has been done on a large scale. We have undertaken such experiments, but some time must elapse before we can give reliable information as to large scale application.

In reply to Professor Whytlaw-Gray: In some cases we have indeed little doubt that the particles precipitated by the process of rapid acoustic coagulation were electrically charged. If, for example, a precipitated aggregate was divided by means of a sharp point, some of the divided aggregate had somewhat strong electric charges. If one moved such charged aggregate through the other aggregates without touching them, forces of attraction and of repulsion could easily be observed. As the experiments on the electric charge of the coagulated, but still suspended, particles are not yet concluded I cannot make any definite statements for this case.

As Professor Whytlaw-Gray points out the aggregates precipitated by the process of rapid acoustic coagulation do exhibit the same structure as those formed in the process of natural coagulation. Since the acoustically produced aggregates are much larger, microscopic study of them may perhaps help to complete the study of the shape of the naturally formed aggregates so successfully made by Professor Whytlaw-Gray and his co-workers.

¹⁰ W. Trabert, *Meteor. Z.*, 1901, 18.

¹¹ W. Findeisen, *Dissertation*, Hamburg, 1931.

¹² O. Brandt and E. Hiedemann, *Kolloid-Z.*, 1936, 75, 129; O. Brandt, *Dissertation*, Köln, 1936.

Mr. A. G. Grant (*Darlington*) said: From the statements just given by Dr. Hiedemann it looks as if the power for sonic aggregation would be of the same order as that required for precipitation. In this case, as some form of removal plant would still be necessary, the merits of sonic aggregation as an industrial process will be determined entirely by the initial cost of the plant involved.

Dr. E. Hiedemann (*Köln*) said, in reply to Professor Andrade: The measurements and kinematographic observations given in our paper were made at a frequency of 10 k.c., though we have made other observations and measurements over the whole range of frequency of some k.c. to some hundred k.c. As the rapidity of the coagulation at 10 k.c. under our experimental conditions is enormous compared with that studied by Andrade and Parker, convection effects were absolutely negligible, so that we did not need to take any precautions against it. Professor Andrade has misunderstood Fig. 4. What he supposes to be actual long particles oriented all in the same direction are not pictures of particles but of the tracks of the coagulated particles when sedimenting. The tracks of falling particles are of course all in the same direction. From the description of our optical arrangement in Fig. 1 it will be seen that the observation was ultramicroscopic. The reason for choosing different times of exposures in Figs. 3a and 3b is stated in our paper so that this question appears also to be due to the misinterpretation.

In calling NH_4Cl - and tobacco smoke particles "dry" we, of course, only wanted to distinguish between really liquid particles (such as oil drops) and particles consisting of or containing solid or nearly solid matter. The nature of tobacco smoke particles is explained when describing Fig. 11. The opinion of Professor Andrade that tobacco smoke particles "are practically all water" has rather surprised me. Mr. E. B. Pearson working in his laboratory has used cigarette smoke.¹³

On page 139 he states that he has used "smoke, dried by being blown through a long calcium chloride tube." If it were true that smoke particles "are practically all water" I am at a loss to understand what remained in Mr. Pearson's smoke after drying it.

Our theory which is here given only in outline will shortly be published in full elsewhere. We will therefore not deal with the remarks on that outline but will only draw attention to some misunderstandings. We have said that the anisodispersity of the medium is an important factor in the process of coagulation at frequencies between some k.c. and about 50 k.c. (determined by the critical relation $r^2 \propto n$). But we have not said that this alone is responsible for the coagulation. For the case of higher supersonic frequencies we have given no theory at all, as we want more experimental results before trying to do so. When I pointed out the importance of the anisodispersity of the medium for the case of higher supersonic frequencies I did not of course mean the coagulation effects due to the anisodispersity, which we treat in our theory and which would be called orthokinetic coagulation in the terminology of Wiegner and Tuorila, as Dr. Sollner has remarked. I directed attention to the fact that the forces of attraction in König's equation used by Professor Andrade are proportional to r^4 . From this I would conclude that no theory which disregards the anisodispersity of the medium can be expected to give very reliable results. I cannot share the opinion of Professor Andrade as to the law of resistance and I shall treat this question very comprehensively in our forthcoming theory. I regret that Professor Andrade has not indicated how it was ensured that the mass-concentration in Mr. Parker's experiments remained constant.

Professor Andrade's chief objection to my serious doubts as to the reliability of his theory is the agreement between his quantitative formula and the experimental results obtained by Mr. Parker. Mr. Parker's

¹³ *Proc. Physic. Soc.*, 1935, **47**, 137.

curve indeed agrees remarkably well with $\frac{dN}{dt}$ proportional to $N^{2/3}$ but, I am troubled by the fact that this formula cannot be derived from Professor Andrade's theory. If one makes the same assumptions as Professor Andrade makes, one really obtains equation (3), but, as a mathematical consequence, one does not get the three next equations given by Professor Andrade. On the contrary mathematical calculations give the following equations :

$$\begin{aligned} -\frac{dN}{N} &= e' N^{1/3} dt \\ dt &= -e' N^{-4/3} dN \\ t &= e'' (N_0^{-1/3} - N^{-1/3}) \end{aligned}$$

and these equations mean that dN/dt is proportional to $N^{4/3}$. This formula violently disagrees with Mr. Parker's results. That Professor Andrade's quantitative formula is not correct can very easily be seen ; if, for instance, t could be calculated from equation (4), he would get t proportional to $N^{4/3}$ instead of $N^{-1/3}$. However, I also regard the hydrodynamic forces as important in the case of higher supersonic frequencies.

MEASUREMENT OF THE OPTICAL DENSITIES OF SMOKE STAINS ON FILTER PAPERS.

BY A. S. G. HILL.

Received 9th March, 1936.

Estimations of atmospheric pollution are made from stains obtained by drawing known volumes of the polluted air through a restricted area of filter paper. The object of the investigation described in this paper was to determine the suitability of employing a photo-electric density meter to obtain a measure of the optical density of these smoke stains, instead of the more usual visual comparative method involving the use of standard stains. It was desired to relate the stain optical density with the mass of the disperse phase in such stains, and so to estimate the smoke concentration.

Method.

A photo-electric density meter, similar to that designed by F. C. Toy¹ was constructed by modifying the original selenium cell form of the instrument.² The selenium cell was replaced by a caesium gas-filled photo-electric cell, with valve amplification. The apparatus is shown diagrammatically in Fig. 1.

Two beams of light from opposite sides of a 6-volt 24-watt electric lamp *L* were diffused by opal screens, and passed through two optical systems to the photo-electric cell *A*. A special shutter *F* enabled the beams (of equal intensity) alternately to illuminate the cell. The photo-electric current produced by the illumination was amplified and balanced as in the usual null method. The stain, the density of which was to be measured, was placed in the path of one beam (at *B*), and a standard neutral optical wedge *W*, connected mechanically to a vernier and scale *V*, graduated in density units, in the path of the other beam of light. The optical wedge was adjusted until the galvanometer *G* gave a null deflection for either

¹ F. C. Toy, *J. Sci. Inst.*, 1927, 4, 369-75.

² *Ibid.*, 1924, 1, 362-5.

position of the shutter. The intensities of the two beams alternately incident on the cell were then equal. The reading on the wedge scale was a measure of the optical density of the stain, the units being dependent on the gradation and density characteristics of the optical wedge chosen. The true optical density D (i.e. the logarithm of the inverse of the transmission to base 10) for the wedge used in these experiments may be expressed in terms of the scale readings as follows:—

$$D = 0.375 (\text{Density Reading} - 0.15) + 0.92.$$

The true optical density of a stain (obtained by subtracting the optical density of the filter paper from that of the paper with stain) was 0.375 times the difference between the respective scale readings.

The stains, obtained on a Whatman filter paper (R.F. special), by means of a hand pump (capacity 180 c.c. per stroke), were circular, and approximately 0.60 cm. in diameter. It is essential that the filter paper should

be of as uniform density as possible, as variations in the transmission of the paper limit the accuracy of the method.

Samples of the particulate cloud to be estimated were drawn through the filter strips by one or more strokes of the pump until a series of stains of varying densities was obtained for measurement with the density meter. The errors due to paper variations were minimised by examining a series of stains in this manner.

Conditions for the use of the photo-electric density meter should be constant. The lamp current

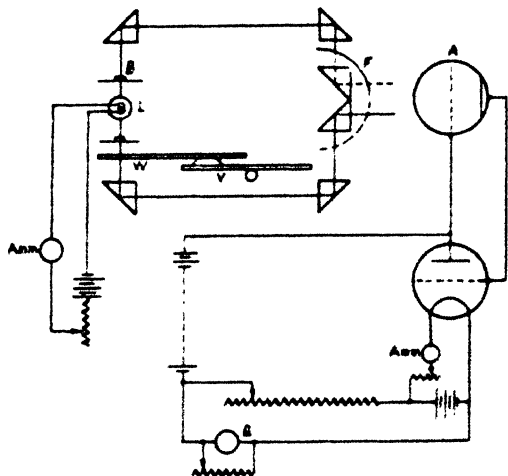


FIG. 1.—Diagrammatic sketch of apparatus.

was maintained at 3.5 amperes, and the valve filament current at 0.25 amperes (Osram D.E. 5B valve, plate voltage 84 volts). After a reasonable time had elapsed for the battery potentials to reach a steady state, the mean optical density of the paper for each strip was measured, and this value used to obtain the optical densities of the respective stains on each filter strip.

A preliminary calibration is necessary for each type of cloud examined. For any given smoke cloud, a series of stains was obtained, and the corresponding concentration of the disperse phase estimated gravimetrically. The concentrations were determined by drawing known volumes of the cloud through small dry asbestos filters, carefully drying the filters, and obtaining the mass increase by means of a balance, sensitive to ± 0.002 mgrm. A calibration curve is thus obtained which gives the relationship between the optical density of the stain and the mass of the disperse phase in the stain and hence the cloud concentration.

The concentration of any cloud of the same substance and characteristics may be estimated from this calibration curve by obtaining a series of stains and determining the stain optical densities. Alternatively, if a known concentration C produces a stain density D for n pump strokes, and an unknown concentration produces a stain with the same optical density D for m pump strokes, it follows that the unknown concentration is $\frac{n}{m}C$, since the mass of the disperse phase in the stain must be identical in the two cases.

Results.

1. Coal Fire Smokes.

A small brazier served as the source of the clouds and was introduced into a chamber (approximate volume, 10 cubic metres), for short intervals of time, depending upon the required concentrations of smoke. Fires emitting various amounts of smoke were employed, and dilutions of any cloud were obtained by the admixture of filtered air. The resulting clouds were fanned continuously while mass estimations and stains were obtained simultaneously.

An examination of the particles constituting the cloud obtained from a moderately smoky fire, as used for stain series No. 4 (Table II.), collected by a sedimentation method, afforded the results shown in Table I., for particles visible under the ordinary microscope. Sub-microscopic particles also were possibly present in these clouds.

Discussion of Results (Coal Fire Smokes).

The relationship between the optical density of stains obtained from coal fire smokes and the mass of the disperse phase in the stains is shown graphically in Fig. 2.

It is somewhat surprising that the clouds from three coal fires burning under different conditions should afford consistent results. Analysis indicated that a very high percentage of carbon was present in these coal fire smokes. Drying the stains had little or no effect on the optical density measurements. The percentage error of the estimation of concentration for individual stains is of the order of ± 10 per cent. This is mainly due to the variations in the optical transmission of the filter paper. Some difficulty was experienced in obtaining a suitable filter paper of uniform transmission, but the percentage error is reduced to less than ± 5 per cent. if a series of stains is obtained and used for the estimation of concentration.

It was found that, with the conditions of these coal fire smoke experiments, the optical transmission of the stain is inversely proportional to the square of the mass of the disperse phase in the stain. It is possible that this relationship exists only for the particular optical arrangement used in the photo-electric density meter. The validity of this method, which is essentially comparative, does not depend upon the accuracy of the optical density measurement.

It is inadvisable to use very dense stains. In practice, it was found necessary to limit the mass of disperse phase in the stain to less than 4.0×10^{-3} grammes. Inconsistent results have been obtained when this amount has been exceeded. These are probably due to factors governing the transmission of light through such stains. The filter may be affected by strain due to the increased resistance to air flow.

2. Owens' Automatic Recording Air Filter.

This photo-electric method of estimating the density of stains on filter paper was considered of interest in connection with automatic filter records.^a Dr. J. S. Owens kindly submitted filter discs with various records for examination.

An atmospheric pollution record (Feb. 12/13, 1934) consisted of forty-five stains of various densities, some of which had been assessed shade numbers by Dr. Owens. The maximum variation in the optical density of the filter paper (without stains) was approximately 0.041. These readings were obtained by avoiding watermarks, print and flaws in the paper, the presence of which near or within the stain area would render

^a J. S. Owens, *Automatic Recording Air Filter: Technical Methods of Chemical Analysis*, G. Lunge and C. A. Keane, Vol. III, p. 645.

TABLE I.—SIZE OF COAL FIRE SMOKE PARTICLES.

Mean diameter of particles (μ)	0.2	0.4	0.8	1.2	1.6
Percentage of particles	22.7	50.2	20.5	5.7	0.9

TABLE II.—OPTICAL DENSITIES OF STAINS FOR COAL FIRE SMOKES.

Cloud Source.		Smoky Fire.			Moderately Smoky Fire.			Clear Fire (little smoke).		
Stain Series Number.		1.	2.	3.	4.	5.	6.	7.	8.	9.
Concentration mgm./cu. metre.		44.4.	25.8.	10.3.	33.0	17.6.	6.9.	20.0.	7.6.	3.1.
Number of Pump Strokes	1	0.30	0.195	0.13	0.20	0.17	0.12	0.19	0.075	0.055
	2	0.48	0.30	—	0.46	0.27	—	0.31	—	—
	3	0.58	0.39	0.26	0.545	0.35	0.18	0.36	0.18	0.13
	4	0.64	—	—	0.64	—	—	0.47	—	—
	5	0.75	0.585	0.375	0.675	0.48	0.20	0.52	0.31	0.165
	7	—	0.675	0.43	—	0.575	0.35	0.585	0.355	0.205
	10	—	—	0.48	—	0.655	0.40	—	0.43	0.24
	15	—	—	0.64	—	—	0.53	—	—	0.32
	20	—	—	—	—	—	0.50	—	—	0.38

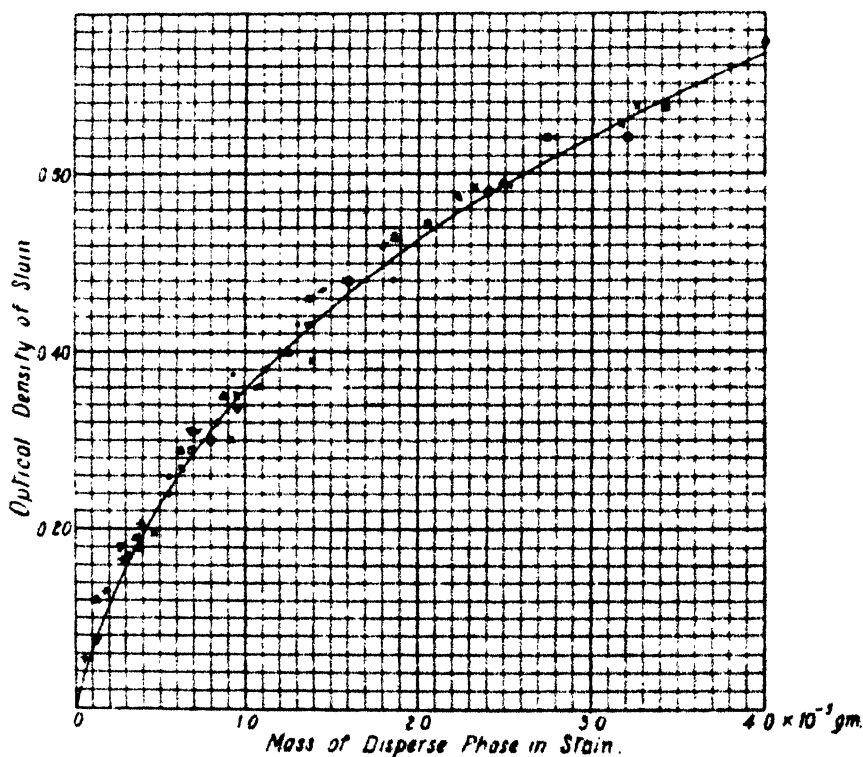


FIG. 2.—Optical density/mass relationship for coal fire smoke stains.

accurate assessment of the optical densities of the stains practically impossible. In the recorder, the filter paper in the region of each stain is subjected to compression. The mean optical density for the compressed areas was 0.026 greater than that for the normal filter paper. This was taken into consideration in estimating the stain densities.

TABLE III.—OWENS' AUTOMATIC RECORDING AIR FILTER RECORD,
DATED 12/2/34.

Stains number 1 to 45 from 00.00 hours.

Stain No. .	1	3	5	7	11	13	15	21	23	25
Optical density .	0.113	0.101	0.064	0.083	0.068	0.071	0.086	0.240	0.248	0.266
Owens' shade number .	4	3	2	2	1.5	1.5	2	10	10	12
Stain No. .	27	29	30	32	33	35	37	40	42	44
Optical density .	0.248	0.266	0.278	0.334	0.413	0.360	0.218	0.135	0.113	0.109
Owens' shade number .	12	13	15	18	20	18	10	5	5	5

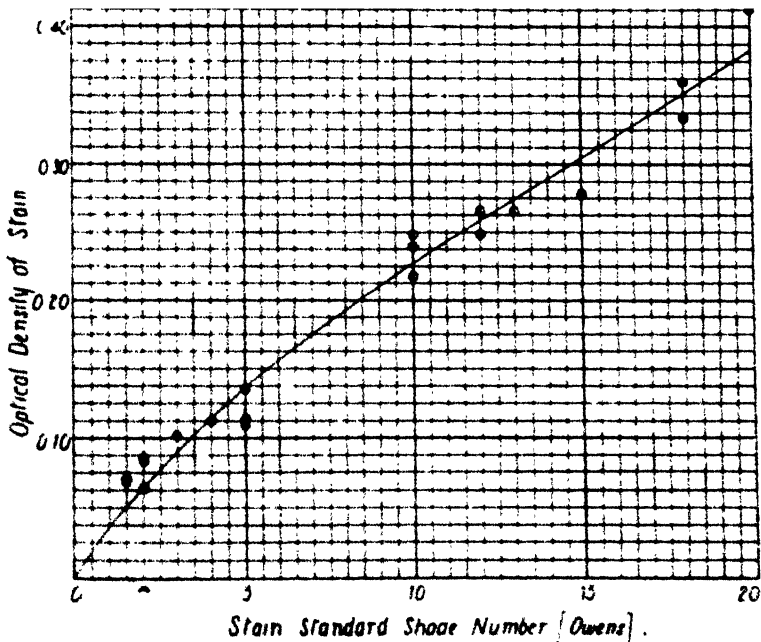


FIG. 3.—Relationship between optical density and shade number for certain atmospheric pollution stains.

The curve showing the relationship between optical density and Owens' shade number, obtained from the results given in Table III., is shown in Fig. 3. It may be observed that the accuracy of the method is of the order of ± 1.5 Owens' shade numbers, the limits of visual assessment presumably being ± 0.5 shade number. The discrepancies shown

in the correlation may be attributed almost wholly to the variation in the optical density of the filter paper used. If a more suitable filter paper were obtainable, having a reasonably constant optical density, a better correlation would result. Alternatively, if it were possible to obtain a larger area of stain, a number of density readings for each stain could be obtained and a mean value would reduce the possible errors of individual readings.

The optical density of the atmospheric pollution stains was more nearly proportional to the mass of the disperse phase in the stain than was the case with coal fire smoke stains. This may be attributed to the different nature of the disperse phase. It is possible that the texture of the filter paper used influences the distribution of the disperse phase in the stain.

The mass of the disperse phase in the Owens' filter stain was compared with that of stains of similar density obtained from coal fire smokes. Owing to the different forms of the two calibration curves, it is not possible to give a constant value for the mass in a stain of unit shade number on the Owens' scale. Thus, a stain of shade number 20 gave an approximate value of 0.29 mgm./cu. metre for unit shade number, while for a stain of shade number 2, a value of 0.26 mgm./cu.m. was obtained for unit shade number. The value given by Dr. Owens for unit shade number is 0.32 mgm./cu. metre.

Although it is not strictly accurate to compare the atmospheric pollution stains with those obtained from coal fire smokes, it may be concluded that the disperse phases in both have much in common, the concentrations required to give a stain of given density being not very different in the two cases.

Application of Calibration Curve to the Estimation of Stain Shade Numbers.

Two filter disc records of atmospheric pollution were supplied by Dr. Owens, the stains of which were not assessed in shade numbers. Density readings were obtained and corresponding shade numbers estimated from the calibration curve. The discs were then returned to Dr. Owens, who kindly assessed his standard shade numbers.

Generally speaking, the results indicated a fair agreement between the visual and photo-electric methods of estimating the stain densities. There appeared to be several anomalous results and, of these, some were definitely attributable to flaws in the paper in or near the stain area. A possible explanation of the remaining cases is that the appearance of the stain by reflected light may not always be a true indication of the mass of the disperse phase in the stain. It is conceivable that an occasional structural variation of the filter may influence the penetration of the disperse phase into the filter. If more of the mass enters the body of the paper, the surface density is decreased and the resulting stain would appear less dense by reflected light than if all the disperse phase remained on or near the filter surface. The photo-electric method, using light transmitted through the stain, would give a measure of the whole mass in the two cases.

Conclusions.

The photo-electric method has proved satisfactory for simple estimations of such coal fire smokes as described. The accuracy of the method is dependent on the uniformity of optical transmission of the filter paper, but with a reasonably good filter paper, and by using a series of stains, the percentage error of estimation of cloud concentration should not exceed ± 5 per cent.

For estimating atmospheric pollution, with the filter discs at present employed, the photo-electric method possesses no advantage over the

visual method. The variations in the texture of the filter papers, and the presence of print, render the photo-electric method liable to error. With a more uniform filter paper, and a larger stain area, the photo-electric method might be used to advantage.

Summary.

A photo-electric density meter has been employed to determine the optical density of stains obtained by drawing known volumes of aerosols through restricted areas of filter paper. The relationship between the optical density of the stains and the mass of disperse phase in them has been determined gravimetrically, and a calibration curve obtained for coal fire smokes. The accuracy of the method is limited by the variations in the optical transmission of the filter paper, but an accuracy of estimation of cloud concentration of ± 5 per cent. has been obtained by utilising a series of stains for each concentration. The method has been applied to the measurement of the optical density of stains of atmospheric pollution obtained with the Owens' Automatic Recording Air Filter. The Owens' shade numbers and the optical densities of the stains have been correlated and the limits of accuracy of the method have been found to be of the order of ± 1.5 standard shade numbers. A comparison with stains from coal fire smokes has indicated a similarity in the nature of the stains. Advantages and disadvantages of the two methods have been discussed.

ON THE RATE OF CHARGING OF DROPLETS BY AN IONIC CURRENT.

BY N. FUCHS, I. PETRJANOFF AND B. ROTZEIG.

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The process of charging floating particles by an ionic current, which plays a very important rôle in the electrical precipitation of smoke and dust, has been the object of a large amount of experimental and theoretical work. This work, however, has been devoted almost exclusively to the study of the final (maximum) charge acquired by the particles in an ionic atmosphere as a function of their size, the applied field-strength, ion concentration, etc. The kinetics of the charging process, on the other hand, have been studied only * by M. Pauthenier ^{1, 2} and by J. P. Gott.³

When the particle is so large that the effects due to diffusion of the ions towards the particle, and to mirror forces, can be neglected, the kinetics of the charging of a spherical dielectric particle can be expressed by the following equation ¹ (assuming that each ion striking the surface of the particle gives up its charge):

$$Q = \left(1 + 2 \frac{k-1}{k+2}\right) E a^2 \left(\frac{\pi n u e l}{1 + \pi n u e l} \right), \quad . \quad . \quad (1)$$

* In the work of Arndt and Kallmann ⁴ we find an investigation of the last stage only of the charging process, when the final charge is practically attained and the rate of charging becomes exceedingly small.

¹ M. M. Pauthenier et M. Moreau-Hanot, *J. de Physique*, 1932, 3, 590.

² Pauthenier et Agostini, *C.R.*, 1934, 199, 705.

³ J. P. Gott, *Proc. Roy. Soc.*, 1933, 142A, 248.

where Q is the charge acquired by the particle in the time t , a the radius, k the dielectric constant of the particle, E the strength of the external electric field, n the number of ions per c.c., u their mobility, and ϵ the electronic charge. For a conducting sphere, the expression $1 + 2\frac{k-1}{k+2}$ becomes equal to 3.

Pauthenier and Agostini² proved the validity of equation (1) experimentally, using 3 to 4 mm. diameter steel balls, falling freely through a cylindrical electric precipitator, parallel to its axis. The field-strength was measured by these authors by means of an incandescent probe, while n was calculated from the equation

$$n = E/4\pi r\epsilon \quad (2)$$

(r distance from the axis of the cylinder). This equation is well known to be valid for the space where the field-strength is constant. The velocity of fall was determined by photographing the balls under intermittent illumination, and the charge acquired by the balls was measured by means of an electrometer. A very close agreement between the theoretical and experimental values of the charge was found.

In the work of J. P. Gott³ the ionic atmosphere was produced by means of X-rays, water drops of 4.4 mm. diameter being used, and only the initial rate of charging was determined. The measurements were considerably less exact than in the work of Pauthenier, but nevertheless quite satisfactory results were obtained.

For particles of the order of 1μ radius and smaller (which it is especially difficult to precipitate in practice), the influence of diffusion of the ions and of mirror-forces may, however, be so considerable that equation (1) must be regarded in this case as giving only the lower limit of the rate of charging. The smaller the particles the larger will be the difference between the actual values of the charge and those calculated from (1).

The theoretical calculation of the rate of charging, taking into account the two above-mentioned factors, seems to be exceedingly difficult. The difficulty is especially increased by the fact that the particles under consideration are of the same order of magnitude as the mean free path of the ions. An experimental study of the kinetics of charging in this region of particle size is therefore indispensable.

The ingenious method employed by Arndt and Kallmann⁴—the direct charging of a droplet by ions within a Millikan chamber, periodically interrupting the ionisation in order to measure the charge acquired meanwhile—allows the use of but relatively small field-strengths and current-densities, i.e., of conditions widely differing from those used in industrial electric precipitation. We chose therefore another method, similar to that of Pauthenier. In this method, a narrow air-jet containing floating particles is passed along the axis of a precipitator and thereupon sucked into an ultramicroscopic cell, where the size and charge of the particles are determined. We further used a cloud of uncharged droplets obtained by condensation of oil-vapours, thus avoiding the charges produced on droplets by spraying. It is clear that the rate of charging of a particle in air of the same velocity as itself will be not different from the rate in still air.

⁴ Arndt und Kallmann, *Z. Physik*, 1926, **35**, 423.

saturated with oil-vapours mixes with the cold air flowing through the tube O. The cloud produced by condensation is thereupon diluted by the air flowing through P, in order to diminish the concentration of droplets. A large amount of oil condensing on the walls of the tubes is tapped off through Q. This oil was then used for the determination of the dielectric constant* (2.56) and the density (0.895) of the droplets. Varying the rate of flow in the tubes O and S and the temperature of the oil, we could obtain clouds of different particle size, with droplets ranging from 0.5μ to 3μ radius. The droplets settling on the walls of the tube J form an oil layer, which continually flows down and appreciably diminishes the width of the orifice. In order to prevent this, the lower part of the tube was constructed as shown in Fig. 1. The rate of flow in all parts of the apparatus was regulated with stop-cocks and measured by flowmeters FF. HH are air-buffers, and M—pressure regulator.

A number of difficulties had to be contended with, in obtaining a steady narrow cloud jet having practically a constant linear velocity for a length considerably in excess of the diameter of the tubes JJ'. Only in this case could the time of passage of the droplets through the ionic atmosphere be determined with sufficient accuracy whilst, at the same time, the distortion of the electric field caused by the tubes could be neglected.

It was found that, for each width of the jet, there exists a corresponding optimal velocity of flow, at which the jet has the maximum of stability. At velocities considerably differing from the optimal, the jet breaks down at a very short distance from the orifice. We found, further, that very narrow jets widen, *i.e.*, their linear velocity decreases markedly with the distance from the orifice. On the other hand, the scattering of the jet by the ionic current made it impossible to increase appreciably the length of the jet, *i.e.*, the gap between the tubes JJ', and therefore, as already said, to use wider jets.

We finally chose a jet of 3.5 mm. diameter and a mean linear velocity of about 3 metres per second. Under these conditions, the cloud jet, observed in the light of an arc-lamp, has sharp boundaries, and its width measured by means of a horizontal microscope remains constant to within 2 to 3 per cent. throughout its length (5.2 cm.). This shows that the linear velocity remains constant to within 4 to 6 per cent. The whole of the jet is sucked without loss into the tube J' of a larger diameter (8 mm.). To prevent loss, the rate of suction must be appreciably larger than the rate of flow of the cloud in J.

It must be noted that there is a definite distribution of velocities within the jet, apparently similar to that of a Poiseuille's flow, but differing from it by the fact that at the boundary the velocity is not equal to zero. An experimental study of this distribution in such a narrow jet seems to be very difficult, and was not undertaken by us. Its general character can be seen from the scattering of the measured values of charges about the mean values (*cf.* below). We limited ourselves to the determination of the average velocity from the rate of flow in the tube J and the cross-section of the jet. From this and from the distance between the tubes JJ', we calculated the average time of passage of droplets through the ionic atmosphere with an accuracy of about 5 per cent., the chief error resulting from inaccuracy in measuring the width of the cloud-jet. The error resulting from the fact that a certain number of ions are sucked into the tube J', where they may also be caught by the droplets, must be exceedingly small, as a rough calculation shows.

The jet is naturally made still less steady by the corona discharge, and is deflected from its straight path and dispersed sooner for stronger and stronger current densities. As it was impossible for the aforesaid reasons to shorten the jet appreciably, we were forced to use relatively

* We are much indebted to Mr. V. Vassiljeff who made this determination for us.

small current-densities up to about 10^{-8} A/sq. cm. The corresponding values of the field-strength and ion-concentration are 1000 V/cm. and 3.5×10^7 /c.c. The deflection and spreading of the jet, resulting from the charges acquired by the droplets, limits the applicability of the method here described to a study of the initial stage of the charging of droplets in an electric precipitator, namely up to about $\frac{1}{4}$ to $\frac{1}{2}$ of the maximum charge.

The use of small current-densities forced us to employ a precipitator considerably larger than the one used at the first stage of this work (12 cm. diameter). With this we were obliged to have a potential on the discharging electrode differing so little from the starting potential, that the slightest fluctuations in the line voltage caused a marked change of the ionic current. In the 31 cm. precipitator the constancy of the current was quite satisfactory.

The density of the ionic current passing through the cloud jet was calculated from the total current flowing through the inner section of the precipitator. In order to ascertain that the current density was constant throughout the circumference of the section, and not changed appreciably by distortion of the field due to the tubes JJ', a rectangular hole 5.2 cm. high and 1 cm. wide was made in the wall of the section C just opposite the cloud jet. A plate made of fine wire-gauze was inserted in the hole providing narrow air-gaps between the plate and the wall. The plate was connected with the galvanometer G. By measuring successively the current flowing through the whole section and through the plate, we found that the ratio of these currents differed from that of the corresponding areas by not more than 3 to 4 per cent. Thus the reliability of the current density values, calculated as mentioned above, was proved. The accuracy of the current-density measurements can also be considered to have the same value of 3 to 4 per cent.

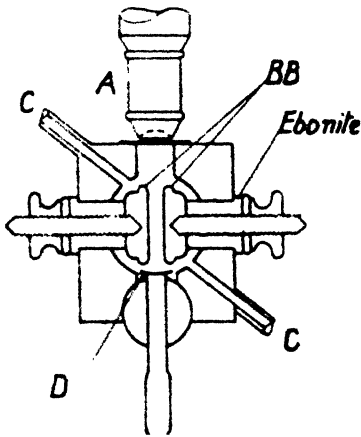


FIG. 2.

Both the size and the charge of droplets were measured in the cell K by the photographic oscillation method worked out in this laboratory* as a development of an ingenious idea of Wells and Gerke.[†] The droplets are allowed to fall under the force of gravity and at the same time they are compelled by an alternating electric field to oscillate in a horizontal direction. Photographing the zig-zag paths of the droplets, we can first determine the size of the droplets from their rate of fall, and then their charge from the horizontal velocity* (cf. Plate I., representing one of the photographs made in this work).

The construction of the cell is shown in Fig. 2. It is made from a massive copper block in order to avoid convection currents. A is the illuminating objective, BB the electrodes producing the horizontal field. The cloud is let in and out through the tubes CC. The adjustable spherical mirror D serves to reflect the illuminating beam back in order to avoid the photophoresis of the droplets. The mean error in the determination of charge by this method is about 2 to 3 per cent. for droplets of radius

* Fuchs und Petrijanoff, *Kolloid-Z.*, 1933, **65**, 171.

† Wells and Gerke, *J. Amer. Chem. Soc.*, 1919, **41**, 312.

* It may be mentioned that in the work of Wells and Gerke one of the motion-components was due not to gravity but to convection or photophoresis. Therefore these authors could determine the charges of droplets only if they knew their size beforehand, or vice versa.

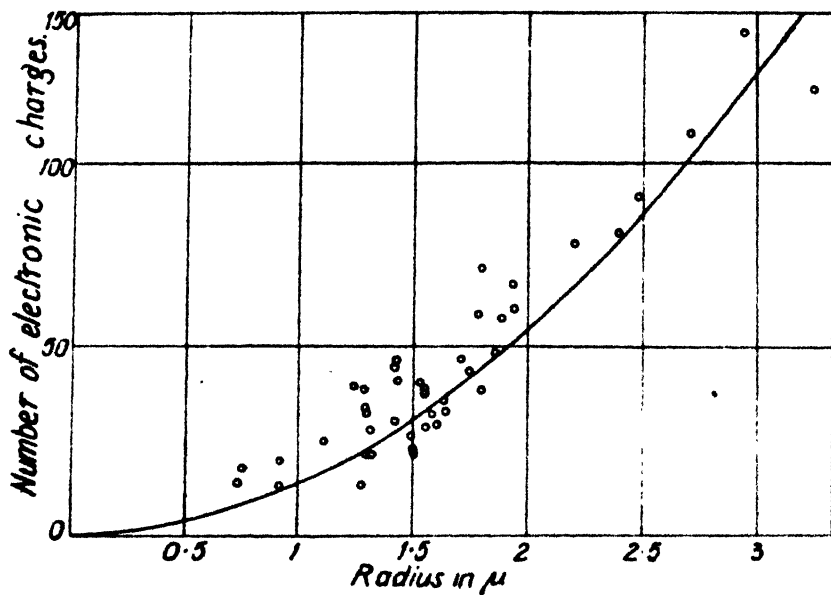


FIG. 3.— $t=0.0165$ sec.; $j=3.18 \times 10^{-9}$ A/sq. cm.; $E=556$ V/cm.; $n=1.98 \times 10^9$ /c.c.

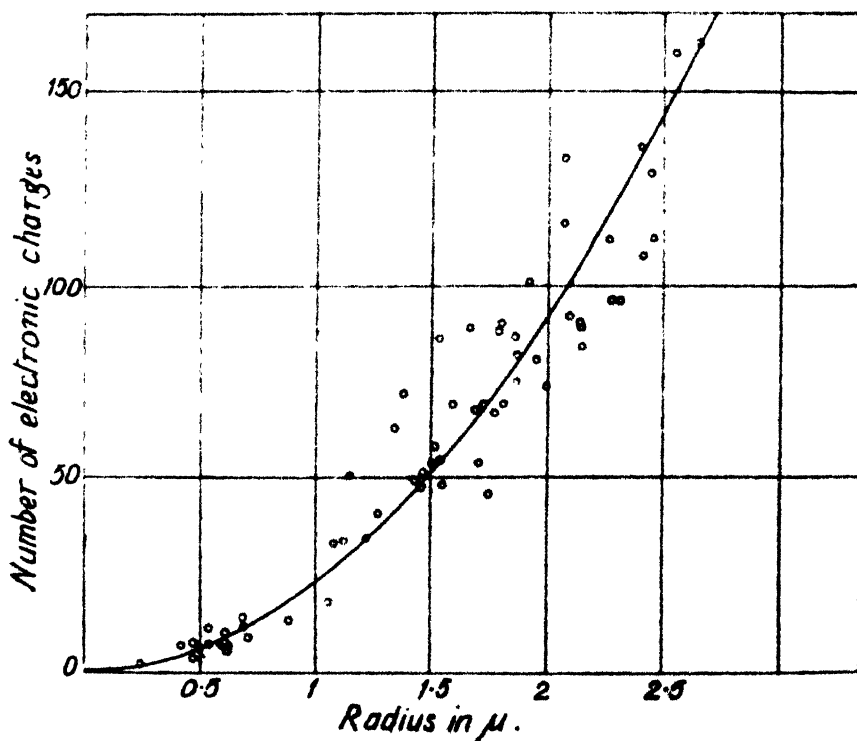


FIG. 4.— $t=0.0172$ sec.; $j=5.51 \times 10^{-9}$ A/sq. cm.; $E=732$ V/cm.; $n=2.70 \times 10^9$ /c.c.

$> 1\mu$ and about 10 per cent. for droplets of 0.6μ radius (due to the Brownian motion). The error in determination of the size is about three times less.

A source of error in these experiments might be expected in the settling out on the walls of the tube J' of more highly charged particles, due to mirror forces and to the mutual electrostatic repulsion between droplets. A rough calculation showed, however, that this circumstance could not have any practical significance under the conditions of our experiments.

The same can be said about the effect due to a screening off of the ionic current by other droplets. As their concentration in the cloud jet was about 10^4 per c.c., the area screened by the droplets of say 2μ radius in a cloud layer 3.5 mm. thick is only

$$\pi \times (2 \times 10^{-4})^2 \times 10^4 \times 0.35 = 4.8 \times 10^{-4}$$

of the total area.

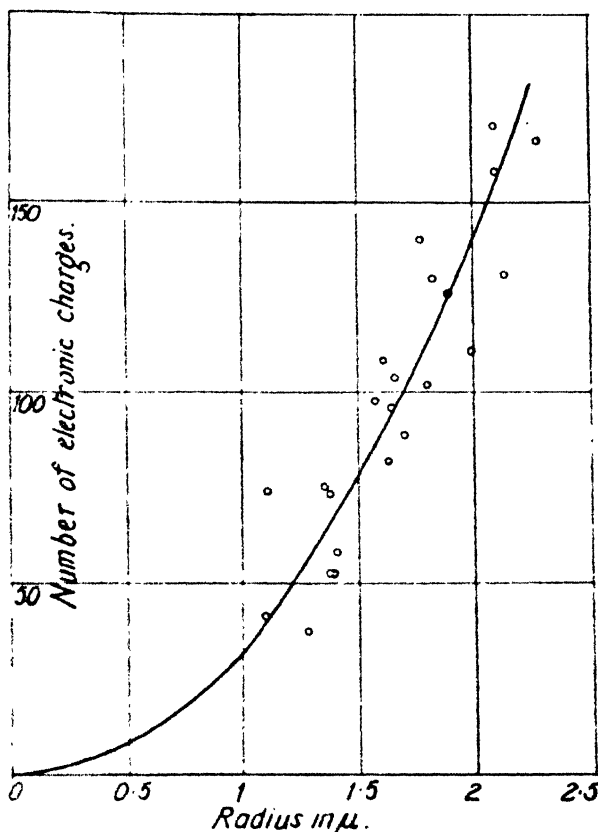


FIG 5.— $t = 0.015$ sec.; $j = 9.1 \times 10^{-9}$ A/sq. cm.; $E = 940$ V/cm.; $n = 3.4 \times 10^7$ /c.c.

Experimental Results.

Some of the results obtained in this work are shown in Figs. 3 to 5. The curves are plotted according to the equation

$$Q = \left(1 + 2 \frac{k-1}{k+2}\right) \pi a^2 j \left(\frac{1}{1 + \pi j/E}\right) \quad (3)$$

derived from (1) by substituting j/E for une . (j = current density). The values of t and j are shown below the figures; k is as large as 2.56 . Taking for the mobility of the ions the value 1.75 cm./sec./V/cm. which gave the best agreement between the theoretical and experimental values of the field-strength in the work of Pauthenier and Moreau-Hanot,¹ we obtain from Townsend's equation,

$$E = \sqrt{\frac{4\pi j r}{u}}$$

corresponding values of field-strength E and ionic concentration n . The error arising from the fact that E was not measured directly, but calculated, could not affect the results appreciably. If, for instance, we take for the mobility the value 1.9 instead of 1.75, the right side of the equation (3) will be reduced only by 1 to 1.5 per cent. The charges acquired by the droplets in these experiments are about 0.2 to 0.3 of the maximum charges.

The experimental points on each curve are taken from several (4-5) photographs. It was very difficult to maintain exactly the same values of ionic current and velocity of the jet in all experiments; they varied as much as about 3 to 4 per cent. In order to be able to put all experimental points on the same diagram, the values of the charges were recalculated according to equation (3).

The scattering of the measured charges about the mean values is due, as already stated to distribution of velocities in the jet, and for smaller particles, besides that to statistical fluctuations.

As can be seen from the diagrams, the mean values of the measured charges lie satisfactorily on theoretical curves. It seems, however, that the data so far obtained are not sufficient to determine definitely how exactly equation (3) holds for the smaller droplets of radius $< 1\mu$. The question will be studied more carefully in this laboratory in the near future.

It must be noted that the method described in this paper is not limited to relatively large particles, whose charge and size can be measured by the "oscillation" or Millikan methods. By measuring the total charge of a cloud by an electrometer and determining the number of particles contained in it, we can measure the charging-rate of particles of any aerosol. This can be accomplished also by measuring the mobility of the charged particles in an electric field provided their size is known.

The method described can be further used to obtain unipolarly charged aerosol with a considerable degree of uniformity of the charges, which is hardly attainable by other methods.⁷

Summary.

1. A method for the determination of the rate of charging of floating particles by an ionic current is described. It consists of passing a narrow cloud-jet parallel to the axis of a cylindrical electric precipitator, and measuring the charges acquired by the particles in it.

2. The experiments were made with oil-droplets ranging from 0.5μ to 3μ radius. The size and charge of the droplets were measured by the "oscillation" method. Current densities of about 3 to 10×10^{-2} A/sq. cm. and times of charging of about 0.01 to 0.02 sec., were used.

3. A good agreement between the mean values of the measured charges and theoretical values calculated neglecting the effects due to diffusion of ions and to mirror-forces, was obtained for the whole range of sizes studied.

We are indebted to the State Gas-Purifying Trust for financing of this work.

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Karpov-Institut of Physical Chemistry,
Moscow.*

⁷ Fuchs und Petrijanoff, *Phys. Chim. Acta of U.S.S.R.*, 1935, 3, 327.

AN EXACT THEORY OF THE COAGULATION OF SPHERICAL PARTICLES ARISING FROM THERMAL AGITATION.

By W. R. HARPER.

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A general theory of coagulation must first deal with its most fundamental aspect—the bringing together of the coagulating particles by thermal agitation. Comparison with experiment is then possible, since this simple mechanism is almost certainly adequate to account for the coagulation of smokes, and appears also to be adequate to account for the coagulation of some colloidal solutions. A theoretical treatment for spherical particles has been given by Smoluchowski,¹ and his results confirmed experimentally by Tuorila, and by Patterson and Cawood. The present author however, has given reasons for doubting the validity of the interpretation of these experiments, and has shown that the theoretical treatment as presented by Smoluchowski is open to serious criticism, being self-contradictory. The coagulation coefficient was obtained by him by a consideration of the diffusion of particles in a concentration gradient which was itself established by the coagulation process, and which was therefore *not* present previous to the coagulation, i.e. not present during the motion which actually determined the rate of coagulation. His treatment might therefore very well give an incorrect value for the coagulation coefficient. Moreover, an alternative treatment of the author's ² (subsequently corrected ³ for a numerical error) gave a value for the coagulation coefficient which was three-quarters that obtained by Smoluchowski. The mathematical methods employed, however, being approximate, could only suggest, and not prove, that Smoluchowski's result was numerically incorrect.

The possible existence of a considerable discrepancy between theory and experiment at the very basis of coagulation theory was a serious matter demanding further investigation, and it was therefore important to determine the true theoretical value of the coagulation coefficient by a method at the same time both logically rigorous and mathematically exact. It is possible to improve the author's previous treatment so as to conform to these standards, and this will be done in the present paper. The result obtained is identical with that of Smoluchowski.

It might therefore be thought to have been more satisfactory to have attempted a reconsideration of Smoluchowski's own treatment, in the hope of obtaining it in a revised form freed from the objections already mentioned. The author has made such an attempt. Further doubtful steps in the argument were thereby revealed, some being concerned with factors of two. At the same time, it did appear that by presenting the argument in a different form, the coagulation coefficient *could* be made to depend on a calculation similar to that of Smoluchowski's, and probably leading to the same value for the coagulation coefficient. Hitherto,

¹ *Z. physik. Chem.*, 1917, **92**, 129.

² *Trans. Faraday Soc.*, 1934, **30**, 636.

³ *Ibid.*, 1935, **31**, 774.

however, the author has not succeeded in obtaining this argument in a form exempt from criticism, so it will not be given here.

The Collision Problem.

If collision always leads to coagulation, the coagulation coefficient may be written down once the frequency with which particles collide is known. It is irrelevant for the purpose of the present calculation whether the collisions leading to coagulation are collisions with contact, or merely approach to within a certain critical distance. We therefore consider a system of points (the centres of the spherical particles) which move along tracks determined by random collisions with the molecules of the surrounding medium, and therefore by the laws of the Brownian movement, and which are said to be in σ collision when they are within a distance σ apart. They are contained in a volume which is very large compared with the probable path of a particle before it suffers a σ collision, so that the collision frequency is the same as for a distribution of infinite extent. If the particles differ in size, we consider the frequency of collisions of particles of a certain size, characterised by centres with a diffusion coefficient D_1 , with particles of another size, characterised by centres with a diffusion coefficient D_2 , their concentrations being n_1 and n_2 respectively. This collision frequency will be unaffected by the presence of the other particles if, as will be assumed, the particulate volume is large compared with the volume of a particle (or its sphere of action).

We are dealing with relatively high concentrations, so a large number of collisions can occur before the concentration is appreciably affected, and the collision frequency must be calculated from what happens during such a time. The initial distribution of each set of particles in space is the distribution at any stage of the coagulation, and has been reached by the processes of diffusion and coagulation. The former leads to a random distribution, and the latter does not disturb it. But the distribution of one set of particles about any particle of the other set, averaged over all such particles, is not random, being disturbed by coagulation. This is because some particles of a random distribution are actually in collision, have therefore coagulated, and really belong to a set of particles characterised by another diffusion coefficient. They must therefore not be included in the averaging. This eliminates all particles of the second set which have particles of the first set closer to them than a distance σ between centres. The required distribution of the centres of the first set about those of the second has therefore zero concentration up to a radius σ . The distribution of the particles of the first set about any eliminated particle of the second set is, however, random outside the radius σ , from which it follows that the required distribution of the centres of the first set about those of the second has a uniform concentration n_1 of randomly distributed centres outside the radius σ .

We may take this initial distribution of centres and use appropriate equations of motion to investigate how long it will be on the average before another collision occurs in the system, from which the collision frequency may be deduced. It is this method which leads to mathematics similar to Smoluchowski's, but we shall not pursue it further, since it is not the most direct line of attack. The result obtained by following it through comes entirely from the initial slight deviation from a random distribution, and therefore depends on a logical subtlety,

since it is clear from physical intuition that the deviation is irrelevant in a direct calculation of the collision frequency, which depends on how quickly the centres move about, and on their average distance apart, and not on their *precise* distribution. That the precise initial distribution is not important will now be proved.

In a direct treatment we have to consider each centre of the second set moving among the first set, calculate its probable lifetime before collision, and average over all the second set. This gives the probable lifetime of a centre of the second set, and hence the collision frequency. Now the departure of the initial distribution from a random one affects the average lifetime before collision in that some second set centres of a random distribution are excluded from the averaging, and to these centres belongs a probable lifetime which is shorter than the average for the random distribution. The true average is therefore longer than the average for a random distribution by an amount which is equal to the difference between the average for the actual distribution and the average for the excluded centres multiplied by the fraction of the centres excluded. The former is of the order of magnitude of the true average, and the latter is equal to the fraction of the centres of the second set which are in collision at any time, which is equal to the volume of a sphere of action of the second set divided by the particulate volume for the first set, and this ratio has been postulated to be very small. We shall, therefore, incur a negligible error by calculating the average lifetime on the assumption that the initial distribution is strictly random. This is actually the case for our two sets of centres if the sphere of radius σ is a pure mathematical fiction, so that, on collision, interpenetration instead of coagulation occurs. Again referring to physical intuition, it is clear that the assumption of interpenetration will not affect the collision frequency, since its magnitude depends on how quickly the centres find each other, and not on what happens during a collision. We shall calculate the collision frequency for a system in which interpenetration occurs.

In spite of what has just been said, it is clear that the rate at which centres find each other is correlated with the time they remain within a distance σ during an *interpenetrating* collision, and we shall now make use of this correlation. Consider any given large volume V , containing $n_1 V$ centres of the first set, each centre being surrounded by a sphere of radius σ . Since the particulate volume is large compared with the volume of such a sphere, the spheres overlap to a negligible extent, and the fraction of the volume V occupied by them is $\frac{4}{3}\pi\sigma^3 n_1 V / V = \frac{4}{3}\pi n_1 \sigma^3$. Now the distribution of the centres of the second set is purely random, so if we consider a particular centre of the second set, the chance that it is located in a particular volume inside V at any time is just the ratio of this volume to the total volume V , irrespective of the position or shape of the volume considered. The probability that the centre of the second set is in σ collision with some centre of the first set at any time is therefore $\frac{4}{3}\pi n_1 \sigma^3$. Another expression for this probability may be obtained from a consideration of the life history of the centre of the second set during a long time T . During this time, it suffers $\nu_2' T$ collisions, where ν_2' is the collision frequency for a single centre of the second set. If the average duration of a collision is τ' it is in collision for a total time $\nu_2' T \tau'$. The fraction of the time it is in collision is $\nu_2' \tau'$, and this is equal to the probability of finding it in collision at any time. We therefore have $\frac{4}{3}\pi n_1 \sigma^3 = \nu_2' \tau'$. The collision frequency ν' for the system is $n_2 \nu_2'$, and is therefore $\frac{4}{3}\pi n_1 n_2 \sigma^3 / \tau'$.

We have now to resolve an ambiguity in the definition of the average duration of a collision. If we consider a centre which comes from infinity to collide with another centre, and then returns to infinity, it is clear that owing to the tortuous nature of its track it will, in general, approach to within a distance σ , and recede to a greater distance several times, thus making a multiple collision. Moreover, the multiplicity will be very high if the mean free path of the centre (between bends in its track) is small compared with σ , as is the case in the present problem. But the probability of return to within the distance σ is only appreciable if the

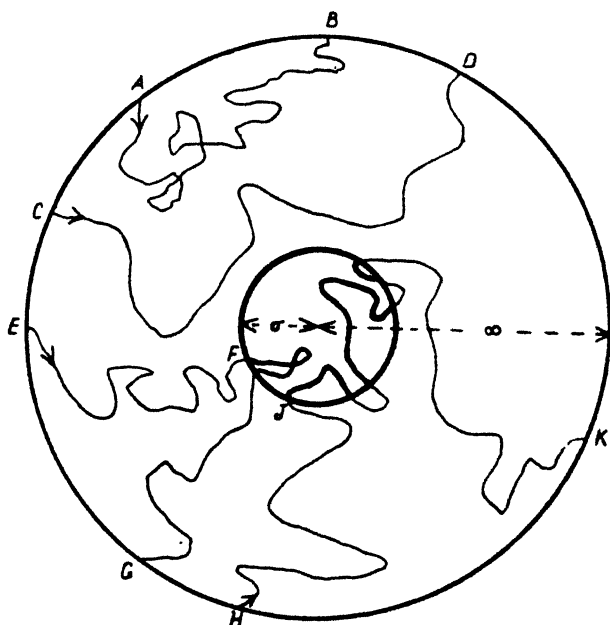


FIG. 1.—AB and CD are tracks which are not members of the subset. EG and HK are two tracks which are members of the subset, HK being a track showing multiplicity in collision. The contribution of these two tracks to the time average comes from the sections within the sphere of radius σ , i.e. from the sections of track which are thickened. The sections of track FG and JK are typical of tracks starting at F and J respectively.

centres have not separated to a distance many times σ , that is, if they have not been likely to have collided with some other centre. When, therefore, the first collision of a multiple collision is sufficient to lead to coagulation, the rest are wasted from that point of view, and the multiple collision counts as a single collision.⁴ What we require, therefore, is the collision frequency in the sense of the number of different centres visited per second, and in calculating the value of τ' we must sum up all the individual times spent within

the distance σ that refer to the different collisions of a multiple collision.

The Case of $D_2 = 0$.

We shall consider first the case of $D_2 = 0$, so that only particles of the first set move. The procedure for calculating the average duration of a collision then reduces to the following, the details of which will perhaps be understood more clearly on reference to Fig. 1, which is purely schematic. We take a sphere of radius σ whose centre corresponds with the centre of a particle of the second set and is therefore fixed, and a set of tracks characterised by a diffusion coefficient D_1 which start at

⁴ The situation is very different if collision does not invariably lead to coagulation. See Fuchs, *Z. physik. Chem.*, 1934, 171A, 199.

random at infinity and return to infinity, and we consider the subset of those tracks which pass through the sphere. We add up the total length of track within the sphere, express it as a time, and divide by the number of tracks in the subset, thus obtaining τ' .

Now the subset is chosen from the set in the following manner. Starting at infinity at the beginning of a track, its course is followed. If it returns to infinity without passing through the sphere it is excluded from the subset. If it reaches any point on the surface of the sphere, it is immediately included in the subset. The sections of track in the subset which lead up to the sphere are therefore not typical of Brownian movement tracks starting at the surface of the sphere, since some of the tracks defined in this way would pass through the sphere, and the actual sections of track do not. But assigning a track in the set to the subset in the manner stated does not affect the completely random nature of the track once it is so assigned, so the sections of track in the subset executed after reaching the sphere are typical of Brownian movement tracks starting at the surface of the sphere, and moreover, they include all the track within the sphere. τ' may therefore be calculated as the average time spent within the sphere by centres starting at a point on its surface and moving along Brownian movement tracks to infinity. When adding up the total time spent by the centres within the sphere and dividing by their number, it is irrelevant which centre contributes which element of time, so we may obtain the average from the distribution of the centres given as a function of the time, without having to follow the detailed history of the individual centres. The distribution function required is that for a set of centres starting together from a point at time $t = 0$, and then diffusing outwards, and is well known.

If Q centres start from the point on the surface of the sphere, and at time t there are $q(t)$ within it, then

$$\tau' = \frac{1}{Q} \int_0^\infty q(t) dt.$$

Now, the number of centres that are situated within a spherical shell defined by r and $r + dr$ whose centre is the starting-point is

$$\frac{Q}{2\sqrt{\pi}} (D_1 t)^{-\frac{3}{2}} r^2 e^{-\frac{r^2}{4D_1 t}} dr.$$

The fraction of these inside the sphere of radius σ is equal to $1/4\pi$ times the solid angle subtended by the spherical cap of intersection of the two spheres at the starting-point, and is $\frac{1}{2} \left(1 - \frac{r}{2\sigma}\right)$. The total number inside the sphere is therefore

$$q(t) = \int_0^{2\sigma} \frac{Q}{4\sqrt{\pi}} (D_1 t)^{-\frac{3}{2}} r^2 \left(1 - \frac{r}{2\sigma}\right) e^{-\frac{r^2}{4D_1 t}} dr,$$

$$\text{and} \quad \tau' = \frac{1}{4\sqrt{\pi}} \int_0^\infty \int_0^{2\sigma} (D_1 t)^{-\frac{3}{2}} r^2 \left(1 - \frac{r}{2\sigma}\right) e^{-\frac{r^2}{4D_1 t}} dt dr = \frac{\sigma^2}{3D_1},$$

whence the collision frequency $\nu' = 4\pi n_1 n_2 \sigma D_1$ for $D_2 = 0$, the value obtained by Smoluchowski.

The General Case.

The earlier approximate treatment of the author gave reason to suppose that the collision frequency for both sets of particles moving

could not be obtained from the case of $D_2 = 0$ merely by substituting $D_1 + D_2$ for D_1 in the formula. It will now, however, be shown that an exact treatment *does* lead to this simple result.

In calculating the average duration of a collision, we have now to allow for the motion of the centres of the second set, that is for the motion of the centre of the sphere of radius σ , or what comes to the same thing, for the motion of the starting-point on its surface. The probability of a particular radial displacement of the starting-point is given by a distribution function of the same form as that used for the motion of the centres of the first set, but with D_1 replaced by D_2 . τ' will now be given by the same integral as before, but with $q(t)$ appropriately averaged. This must be done by taking the number of centres of the first set which are within the sphere of radius σ when the starting-point has suffered a given displacement, multiplying by the probability of the displacement, and integrating over all possible displacements. A detailed integration has been carried out along these lines, and leads to the conclusion already stated. It will, however, not be given here, since it is lengthy, and since the same conclusion can be reached by the following general argument.

It is clear that the integral for τ' is correctly modified to allow for the motion of the starting-point if instead of expressing it in terms of the probability of a given displacement of a centre of the first set relative to a fixed origin, we use the probability of a given displacement of a centre of the first set relative to a centre of the second. It was proved by Smoluchowski¹ as part of his own treatment that this probability is given by a formula which is the same as the one originally used except for the substitution of $D_1 + D_2$ for D_1 . This substitution will lead to the same change in the formula for τ' , so the general collision frequency will be $\nu' = 4\pi n_1 n_2 \sigma (D_1 + D_2)$.

Summary and Conclusions.

It has been shown that whereas the criticisms advanced elsewhere by the author against the theoretical treatment of Smoluchowski remain justified, an exact treatment leads to precisely the same formulæ, thus contradicting the indications of the author's previous approximate treatment. It follows that the theory of the effect of heterogeneity given by Smoluchowski requires no modification.

The theory, however, is only applicable to spherical particles coagulating to give spherical particles, and as pointed out in the author's previous paper, a departure from these conditions must lead to a marked change in the coagulation coefficient. The agreement between the calculated rate of coagulation for particles which coalesce on coagulation so as to form new spherical particles, and the observed rate for oleic acid smokes, must now be taken as showing that the different cohesive forces for different orientations of the long chain compound do not have the result of deforming the droplets appreciably from the spherical shape, and that even if an adsorbed surface layer does prevent true coalescence on coagulation, yet the resultant complex droplet is deformed into a shape which is nearly spherical. The further agreement with the observed rate of coagulation of stearic acid smokes must be taken as showing that the stearic acid is a super-cooled liquid in the early stages of the coagulation, even though it is solid in the later stages. It is unfortunate that experimental evidence is not available to check these conclusions directly.

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GENERAL DISCUSSION.*

Professor R. Whytlaw-Gray (*Leeds*) said: Experimental evidence suggests that the rate of coagulation is not greatly influenced by the shape of the particles. The constants for smokes of stearic and oleic acids agree closely with theory whilst that for ferric oxide of the same weight concentration is only 30 per cent. greater. When these smokes are allowed to coagulate until the particles are large enough to be seen with the microscope, the stearic acid complexes, though not truly spherical, are of a compact form, whilst those of ferric oxide are loosely built, chain-like structures, formed of units which appear like beads on curly strings.

The difference in structure of the two types is striking and if the ultramicroscopic particles possess the same form as those of microscopic dimensions, it is surprising that the coagulation constants for the two smokes do not show a greater divergence.

It is therefore evident either that the form of the particles has a relatively small effect on the coagulation rate, or that the ultramicroscopic particles even in a smoke like ferric oxide, with such a marked tendency to chain formation, are spherical in the early stages. Examination by X-ray or electron diffraction methods might enable the size of the units in these aggregates to be estimated and thus throw light on this question.

Mr. W. Barrett (*Gerrard's Cross*) said: In the equation $dn/dt = -Kn^2$, K has the dimensions of (frequency) \times (volume). This suggests that there may be a fundamental frequency, but nothing of the kind seems to appear. For purposes of extrapolation it would seem preferable to use the form $dn/dt = -Kn(n - 1/V)$ where V is the volume occupied by the smoke. The integral of this is

$$\frac{1}{nV} = 1 - e^{-\frac{Kt}{V}}$$

which does not, as the classical equation, lead to a value less than unity for the total number of particles at the end of infinite time. The curve is tangential to $1/n = Kt$ at the origin and asymptotic to $nV = 1$ at infinity.

Professor J. C. Phillip (*London*) said: Is it not possible that the gap between the molecular state and that of the "primary particles" is associated with the high curvature of extremely small droplets (particles) and the correspondingly high vapour pressure?

Mr. A. G. Grant (*communicated*): Dr. Fuchs' paper is the only one in this section applying specifically to electrical precipitation phenomena, and I have endeavoured to compare the authors' results with values obtaining in full scale plant working.

The charging of a particle in an electric field is in effect the collection of electronic charges up to a saturation value determined by the dielectric constant and radius of the particle and the strength of the field. Millikan in his Oil Drop Apparatus has demonstrated that in a feebly ionised field, the rate of electron charge collection is relatively small, and in fact he was able to study the successive addition of small numbers of electrons.

In the more strongly ionised fields obtaining in electrical precipitation, it has generally been assumed that a particle acquires its saturation charge in negligible time, this charge being given by the first half of expression (1) in the authors' paper. The authors have now demonstrated that a measurable time is required to reach saturation in accordance with the correction applied by the expression $\frac{\pi n u e t}{1 + \pi n u e t}$.

In their experiments only 30 per cent. of the maximum charge was reached in the measurable time of approximately 0.02 seconds. It is to be regretted that they were not able to make determinations and to plot

* On the three preceding papers.

results for a wider range of times, as their work resolves itself into a single point determination—that is, we now know only that expression (1) is correct for complete saturation when the value of time is relatively great, and for partial saturation at the one time, 0.02 seconds. Nevertheless we can probably assume the validity of the time correction.

Now, whilst in precipitation work, values vary over a wide range, I think we can take, as typical lower values, a field strength of a thousand volts per centimetre, and an ion concentration of 10^8 per c.c. These figures are respectively twice and ten times those used by the authors. We can retain their particle radius of the order μ . Inserting these values in their expression for particle charge, we obtain altogether higher degrees of charging. For times of 0.5 seconds upwards, the departure from saturation is negligible. At 0.05 seconds the degree of saturation is 80 per cent.

In precipitation work, I think we can say that 0.5 seconds is the lower limit for time of contact of a particle in the ionising field. In this time and for values I have just assumed, 97.5 per cent. of the maximum charge is acquired by the particle. It thus appears that the authors' work in establishing the validity of the time correction has enabled us to show that in ordinary precipitation work the time factor can be ignored; that the earlier assumption, though without justification, that precipitation calculations can be made on the basis of a fully charged particle, was in fact correct.

I think an explanation is easy to find. The velocity of a particle in the electric field varies directly as its charge, so that a 50 per cent. charged particle will be precipitated in double the time required by a fully charged one. Thus time for removal is a function of charge, and charge is a function of time. Now since removal time is large, compared with the required charging time, it automatically follows that a field so designed as to remove the particle, will automatically give it its saturation charge.

This paper is of very great practical value as being, to my knowledge, the first successful attempt to determine the time factor under controlled conditions, and I hope that my remarks will not be taken by the authors to imply that their work has been other than constructive.

Dr. N. Fuchs (Moscow) (communicated): I cannot agree with the objections to the theoretical treatment of coagulation given by Smoluchowski which are put forward by Mr. Harper. The deduction of Smoluchowski can be presented in a form which does not require the explicit use of a "concentration gradient," attacked by Mr. Harper, and approaches the treatment given by Mr. Harper himself.

Let $W(x, y, z, t)$ be the probability that a material point with co-ordinates x, y, z , performing the Brownian movement will cross a certain immovable surface at least once during time t . Kholmogoroff¹ showed that W must satisfy the Einstein-Fokker equation

$$\frac{\partial W}{\partial t} = D \Delta W. \quad (1)$$

In the case of a spherical surface with radius σ , W depends only on the distance r between the material point and the centre of the sphere, and equation (1) takes the form

$$\frac{\partial W}{\partial t} = D \left(\frac{2}{r} \frac{\partial W}{\partial r} + \frac{\partial^2 W}{\partial r^2} \right). \quad (2)$$

From the physical significance of $W(r, t)$ it is clear that $W(\sigma, t) = 1$ when $t > 0$, and $W(r, 0) = 0$ when $r > \sigma$. The solution of (2) is therefore:

$$W(r, t) = \frac{\sigma}{r} - \frac{2\sigma}{r\sqrt{\pi}} \int_0^{\frac{r-\sigma}{2\sqrt{Dt}}} e^{-z^2} dz. \quad (3)$$

¹ Kholmogoroff and Leontowitch, *Physik. Z. Sowjetunion*, 1933, 4, 1.

We have thus obtained an expression for the probability that a material point (whose distance from the centre of a sphere σ is r) will cross its surface at least once in time t . If at the moment $t = 0$ the spheres σ are distributed at random with the mean concentration n , there will be $4\pi r^2 n dr$ of them within a spherical shell defined by r and $r + dr$, whose centre is the initial position of the material point, and the point will cross in time t the surface of as many as

$$dI = 4\pi W(r, t) nr^2 dr$$

spheres.

The total number of the spheres crossed will be :

$$I = 4\pi n \int_{\sigma}^{\infty} W(r, t) r^2 dr. \quad . \quad . \quad . \quad (4)$$

In unit time it gives

$$\frac{dI}{dt} = 4\pi n D \left(1 + \frac{\sigma}{\sqrt{\pi D t}} \right) \quad . \quad . \quad . \quad (5)$$

and that is exactly the equation obtained by Smoluchowski. It differs from that deduced by Harper by the factor $1 + \frac{\sigma}{\sqrt{\pi D t}}$, which rapidly approaches unity. The physical significance of this factor is obvious : in our deduction we counted only the spheres crossed by the material point the first time, and did not pay any attention to the subsequent crossings of the same sphere. At the beginning of the process the point is surrounded by those spheres which it has not yet crossed and, therefore, the number of registered crossings in unit time is larger than later on, when a certain stationary distribution of spheres, which have already been crossed, is established around the point. In the treatment given by Harper which is based on averaging the time spent by the material point within a single sphere this circumstance is omitted.

The deduction cited above shows that the theory of coagulation given by Smoluchowski is correct in all cases where equation (1) is valid, *i.e.* when the radius of the particles is large in comparison with their "apparent mean free path."³ If this condition is not satisfied, a correction for the "concentration drop" at the surface of the spheres σ , diminishing the rate of coagulation, must be introduced in the equation (5). This drop is quite similar to the well-known temperature-drop and velocity-drop (slip) at the surface of small spheres in gaseous media, and was taken into account for the first time by Townsend³ in his theory of diffusion of ions towards small conducting spheres. For particles of 10^{-5} cm. radius this correction makes a difference of only few per cent., but for 10^{-6} cm. particles it is already very considerable.⁴

In reply to Mr. Grant (*communicated*): I must emphasise, that our work is substantially a further development of the excellent work of M. Pauthenier and co-workers cited in our paper.

The chief result obtained in our laboratory is that the charging-equation derived and experimentally tested by Pauthenier over a wide range of time remains exactly valid for small particles. Although this result was obtained for a small range of time (0.01-0.02 sec.) only, there remains little doubt as to its applicability over the whole range of the charging.

On the other hand it seems that the applicability of Pauthenier's equation to small particles ($\sim 1\mu$) is limited to comparatively large values of the field-strength as used in electric precipitators. In a weak field the effect due to the diffusion of ions can by no means be neglected.

³ Smoluchowski, *Annal. Physik.*, 1906, **21**, 769.

³ Townsend, *Electricity in Gases*, Chapter 6, 1915.

⁴ Fuchs, *Z. physik. Chem.*, 1934, **171**, 199.

Dr. W. R. Harper (*Bristol*), in reply (*communicated*): I may appear to be excessively insistent on mathematical rigour, but there is good reason for it. In developing my own treatment a certain step in the argument seemed mathematically obvious not merely to myself but to others whom I consulted. Moreover there was a proof to justify it. Nevertheless it subsequently appeared that the proof was faulty and that what had seemed obvious required changing by a factor of two. I conclude that the result of any treatment is only to be trusted when obtained by flawless reasoning.

Doubts of this nature concerning the treatment of Dr. Fuchs restrained me from taking the initiative in discussing it, but I would now say that his treatment seems to me to be perfectly rigid with one proviso and one exception. The proviso is that the treatment be presented as a calculation of the collision frequency in a system of interpenetrating spheres as in my own treatment, and subsequently applied to the actual coagulation problem with the justification therein given. We can then choose one centre out of the system and follow its track from $t = 0$ to $t = \infty$, calculating how many spheres it intersects per second, and avoid having to picture it as possessing the incompatible properties of being able to collide with a number of spheres without changing its identity, and becoming a different particle after each collision. It is ensured that multiple collisions are counted as single by working with the probability that each surface is crossed at least once, and by neglecting the initial part of the solution. A comparison of the initial form with the ultimate form of the solution now shows that the multiplicity of a collision must be infinite, it being presupposed however that the mean free path of the centre is infinitesimally small, its track velocity being of course infinite to give a finite diffusion coefficient.

The apparently innocent assumption that $W(\sigma, t) = 1$ for $t > 0$ appears to me to require proof, and this is not given in the work of Kholmogoroff referred to. For it to be correct, a centre starting infinitely near a plane surface cannot move to a finite distance from the surface without crossing it at least once, and it would seem pre-supposed that the mean free path is to be taken as an infinitesimal of the second order, since we are considering Brownian motion and not a phenomenon dependent on track velocity. We may magnify the picture and conclude that the assumption is only correct if a centre starting at a finite distance from an infinite plane surface and executing Brownian motion with an infinitesimally small mean free path cannot move to infinity without crossing the surface. Whether or not this is so, seems to me to be by no means obvious, but it must be so since Dr. Fuchs and I obtain the same value for the coagulation coefficient.

I cannot admit that the treatment of Dr. Fuchs disposes of my objections to the treatment of Smoluchowski—I would say rather that it avoids them. It is difficult to decide from the original papers of Smoluchowski just what significance he intended to be attached to his mathematics, but from the formulation in the *Zeitschrift für Physikalische Chemie*, it seems clear that the colloid particle is to be regarded as analogous to a large sphere on which particles of vapour are being condensed, in which case the objection that the colloid particle has coagulated before even the establishment of the boundary conditions which lead to the solution of the problem for the large sphere can be made precise, and is surely valid. I now see however that this objection and others can most simply be met by again presenting the mathematics as a derivation of the collision frequency for a system of interpenetrating spheres and then applying the result to coagulation with the appropriate justification, instead of presenting it as a direct calculation of the rate of coagulation. We choose one sphere out of the system at time $t = 0$, and calculate for all subsequent time how many centres cross its surface per second for the first time. This clearly gives the collision frequency for the sphere if multiple collisions are counted as single collisions, except that the initial part of the solution must again be neglected because we are then counting some collisions which really belong to

time previous to $t = 0$. Smoluchowski's method of calculating the number of first arrivals is of course to solve the diffusion equation with the appropriate initial conditions and the boundary condition of zero concentration. He justifies this on the ground that it works for the particular case of a plane surface, from which one may conclude that he regarded it as plausible but unproven that it is correct in the general case. It may however be proved in the following way: Consider any initial distribution of centres in space situated on one side of any closed surface. It is required to find the mean number of centres that will have crossed the surface at least once in time t . This is equal to the number that would have been removed from the distribution if the surface annihilated them on arrival. The annihilation may be carried out by creating a negative centre when and where a (positive) centre arrives at the surface, but otherwise allowing both sets of centres to diffuse unimpeded by the surface. The distribution of both positive and negative centres is governed by the diffusion equation, so the actual distribution of centres (with annihilation at the surface), being the difference between these distributions, is also a solution of the diffusion equation. That it is the solution with concentration at the surface put equal to zero follows from the fact that if it were not, there would be maintained a concentration discontinuity at the surface (the concentration inside being *ex hypothesi* zero), which would result in an infinite rate of removal of centres from the distribution, and this could not be maintained.

The treatment of Smoluchowski can therefore be presented in a mathematically rigorous form leading to the usual result. It can, moreover, be transformed into my own formulation, thus providing a cross check. We may therefore conclude that there is now no doubt whatsoever about the value of the coagulation coefficient.

INTRODUCTORY PAPER, PART I.(b) THE GENERAL PROPERTIES AND BEHAVIOUR OF DISPERSE SYSTEMS CONSISTING OF AQUEOUS AND OTHER VOLATILE PARTICLES, *i.e.* MIST, CLOUD, HYGROSCOPIC NUCLEI, TOWN AND COUNTRY FOGS.

BY G. M. B. DOBSON.

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Meteorological Aspects.

I have been asked by the Council to give a short introductory talk on the meteorological aspects of Dust, Smoke, and Fog. I think that it will be best if I try to give a very brief résumé of our knowledge of this subject at the present time, and thereby to reveal where our ignorance is greatest and where more work is particularly wanted.

With regard to atmospheric haze and fog—whether in country or town—the main physical principles appear to be known, but there is much that requires further elucidation. In clear air, free from fog, there are always present a large number of minute particles, some of which are hygroscopic, while others are not so. In country districts, particularly near the sea, the hygroscopic particles may be largely sea salt derived from sea spray, while in towns, those due to combustion of fuel, such as droplets of H_2SO_4 , will probably outnumber the others.

It has been suggested that nuclei are formed by sunlight, but this does not seem to be certain.

These hygroscopic particles will condense upon themselves an amount of water depending on the relative humidity of the surrounding air, until they are in equilibrium and their vapour pressure is equal to that in the air. Their size will thus vary with the relative humidity, while their number remains constant. Thus the visibility will depend on the relative humidity as was shown by Aitken. On the other hand, the non-hygroscopic particles will remain constant in size and add an amount to the haziness which is independent of relative humidity.

Many of these minute particles can be seen in the ultra-microscope (possibly all, if the illumination be good enough), and if arrangements be made to saturate the air and cool it by a slight expansion, the condensation of water upon them is immediately seen. The particles are clearly of all sizes, and so far as I have seen, most of them seem to have water condensed on them at a supersaturation of 1 or 2 per cent. forming droplets. An estimate of the size of individual particles can be made from the magnitude of their Brownian motion. The particles appear to have a radius of a few times 10^{-6} cm. The smaller particles therefore scatter light to an extent which depends on the inverse fourth power of the wave-length of the light and on the sixth power of the radius of the scattering particle. (Owing to this sixth power law, the smallest particles are very difficult to see in the ultra-microscope and, judging by the brightness, the particles appear to vary in size more than they really do.) On the other hand, the larger particles scatter all wave-lengths alike, hence the increasing whiteness of the sky in hazy conditions.

When the humidity approaches saturation, a large amount of water will condense on the hygroscopic particles, their equilibrium being governed by the opposing effects of surface tension and osmotic pressure. If these two alone determine the size of the drop, it must pass through an unstable size, and as the relative humidity increases, it would slowly grow, and at some point suddenly jump to a much bigger diameter. There are, however, two other things of which we must take account, firstly the removal of water vapour from the air by condensation on the drop, and secondly the effect of latent heat of water. It can be shown that if the initial hygroscopic particles are sufficiently large and numerous, the effect of the removal of water vapour may prevent any unstable growth, while the effect of the latent heat set free, must tend to prevent any sudden condensation.

That only a small number of the original nuclei grow into fog droplets during a fog, is easily seen in the ultramicroscope, where the relatively large fog droplets are seen like brilliant stars falling across the field of view, and at the same time a far larger number of the minute particles are seen, such as are present when there is no fog. This, of course, is what theory would lead us to expect, as the largest hygroscopic particles would first grow into fog droplets, and, only after these were removed, would the smaller particles increase greatly in size. This should make us reflect whether we are making the best observations for meteorological purposes if we measure the total number of hygroscopic particles present in the air as we do with the Aitken Counter. Should we get a more useful measure for meteorological purposes if we counted only the number of particles which condensed water sufficiently easily to form nuclei for fog and rain drops? This number is probably much smaller than the number counted by the Aitken apparatus. The difficulty

would be that there are probably particles of all types present in any sample of air, forming a continuous series, and we should have to draw some arbitrary line between those that readily act as condensation centres, and those which require some considerable supersaturation.

It is clear that the relative humidity must be approximately 100 per cent. in a fog, but it is not certain whether it may be a little above or below this value. From the effect of surface tension we should expect it to be slightly above 100 per cent. but it seems possible that the droplets and nuclei may be cooled by radiations slightly below the temperature of the surrounding air, so that they will be in equilibrium at a relative humidity slightly below 100 per cent.

The processes taking place after the fog has formed, are not entirely clear. If the hygroscopic nuclei are of such a size that there is an unstable period in their growth, and if cooling continues slowly in air already at 100 per cent. R.H., one would expect the excess water vapour to condense out on the existing droplets, so that these would increase in size, but there would be little increase in the number of droplets, unless those initially formed had fallen out of the air. On the other hand, if the hygroscopic nuclei are so large and numerous that there is no unstable period in their growth, the larger ones might become stable, and condensation occur on those slightly smaller. Which of these represents the facts in nature I do not know, possibly one in clean country air, and the other in towns. Certainly as a fog gets thicker, the number of droplets appears to increase.

It has been stated that the sizes of fog droplets fall into definite groups, so that those of one group may be explained as due to the combination of two drops of a group with smaller size. Again measurements have been given showing that while drops of all sizes within a wide range are present in any fog, there is in any given fog a particular radius which is most common, and that this radius is always a whole multiple of a certain value. Before the meteorological world will accept any of these views, they will clearly require many more observations.

The fog droplets being of the order of a few microns in radius, scatter all wave-lengths of light alike, hence the sun seen through a country fog appears white, and it is only in a town fog where there may be a large number of minute particles in addition to the water droplets, that the sun may appear red in a fog. This shows that the benefit to be expected from coloured lights when driving in a fog is negligible.

It seems probable that electrical conditions have no appreciable effect on the equilibrium of fog particles. That mobile ions are caught on the fog droplets is well known, the conductivity of the air thereby being greatly reduced, causing the great increase in the electric potential gradient usually observed in a fog.

The conditions when a fog evaporates, will be largely the reverse of those when it forms, except for two things. Firstly as we have already said, the temperature of the particle may not be exactly that of the surrounding air, and secondly, in towns, the solution of SO_2 in the fog droplets and its slow oxidation into SO_3 may lead to the evaporating droplet being a dilute solution of H_2SO_4 when the droplet will be stable at a lower relative humidity than that at which it was formed. There seem to be few observations to guide us here.

I would call the attention of workers in this field to the value of observations made with ultra-microscopic methods. These may be made either in small glass cells as described by Professor Whytelaw-Gray or,

for use in the free air, they may be much larger. It is quite possible to arrange an intense beam of light with suitable diaphragms, so that the light scattered from the beam by pure dust-free air can be seen. In such an apparatus the small particles present in non-foggy air are seen and their rate of growth with increasing relative humidity can be studied. The advent of the new high pressure mercury vapour lamp shortly to be placed on the market, should make the ultra-microscopic method of much greater value still. A great advantage of the ultra-microscopic method is that the particles and droplets are studied with the minimum of alteration from their natural conditions, and each particle can be dealt with separately, without making any assumption that all particles are alike.

Passing to the removal of particulate matter from the atmosphere, presumably washing out by rain, plays a large part, but our knowledge is very scanty indeed. For instance, is the removal due to the washing action of rain as it falls through the atmosphere or is most of the particulate matter brought down by rain caught at the moment of condensation within the cloud?

We are equally ignorant about the distribution of particulate matter. Thus, how does the pollution produced by a town fall off with distance from the town, under different conditions?

Finally, what is the effect of particulate matter in the atmosphere in cutting off sunlight and daylight? Particularly what is its effect within large cities? Is the decrease of light approximately the same for all wave-lengths, or are there sufficient very small particles in city air to make the reduction of the short wave-lengths much greater than that of the long wave-lengths? Measurements have shown that ultra-violet light may be reduced at the centre of a town, to half the intensity of that received in the suburbs, but such measurements are unfortunately few, and these frequently refer to one band of wave-lengths only.

The discussion of these matters now to take place, is certain to be of great interest, and I hope, will act as a stimulus to still further work on the subject, which is really one of extraordinary importance to the community as a whole.

Oxford.

THE NUCLEUS IN AND THE GROWTH OF HYGROSCOPIC DROPLETS.

BY HILDING KÖHLER (*Uppsala*).

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The nature of the nuclei of which a cloud is really formed can best be investigated through the droplets of which the cloud is composed. Such an investigation generally presents great difficulty. After long microscopic investigations I proved that the ice which, in fog, is deposited on mountains as frost is formed through the undercooling of water droplets. The difficulties have thus been reduced to an analysis of such masses of ice.

Since the investigations of Melander and Lüdeling it has been sup-

posed that sea-salts can serve as nuclei of cloud condensation ; that this must be the case has recently been proved by J. H. Coste and H. L. Wright.

From 1919 to 1923 (independently of earlier suppositions) I carried out (on the Haldde) analyses of hoar-frost for chlorine content, on the supposition that sea salts were nuclei of cloud condensation, and at the same time measured the size of the droplets in the fog from which it was deposited.

A. Chlorine.—Generally about 2 kg. of hoar-frost, collected with precautions against contamination, were evaporated to 100 c.c., and the chlorine content determined by Mohr's method of titration.

B. The size of the droplets in fogs or clouds was measured optically. A projector with an arc-lamp and a parabolic mirror sent parallel rays to the observer 61·8 m. away. The coronæ in the space-grating formed by the droplets were measured. From the radius of these coronæ the radii of the droplets were measured according to the well-known formulæ :—

$$r = \frac{1 \cdot 220 \cdot \lambda}{2 \sin \theta_1} ; r = \frac{2 \cdot 233 \cdot \lambda}{2 \sin \theta_2} ; r = \frac{3 \cdot 238 \cdot \lambda}{2 \sin \theta_3},$$

where θ is the angular radius of the first (θ_1), second (θ_2) and third (θ_3) coronæ, measured at the outer line of the violet colours, and λ is the so-called "wave-length of white light" ($0 \cdot 571 \mu$). The clearness of the coronæ depends on the homogeneity of the cloud. If a certain size of droplets sufficiently outnumbered all others we get measurable coronæ. The more homogeneous the cloud, the clearer are the coronæ, the more distinct the limits ; with a preponderance of drops of a certain size very distinct limits are observed.

Lichen spores were used to give frequency curves of different standard degrees of deviation grouped around an average size. Measurements of the coronæ given by these spore clouds showed that the spores had dimensions which corresponded with a great accuracy with the average values microscopically measured.¹ If the standard deviation was great (as for instance in the case of purchased Lycopodium spores), the coronæ became pale and indistinct, since the white colour is dispersed over the different colours, although even in this case the measurements of coronæ gave the size of those spores which are present in the greatest quantity.

By measurements of coronæ in fogs there is thus obtained, the size of those droplets which are in the majority within the field of observation. If very dissimilar droplets are present to the same extent the coronæ become very indistinct ; according to my experience this is often the case with low-land fogs, and sometimes occurs also in clouds and mountain fogs. No coronæ at all may arise, if the fog is sufficiently inhomogeneous and no one size preponderates. A single well-performed measurement of coronæ gives a more reliable value than several millions of measurements of separate droplets.

Results.

1. The most commonly occurring chlorine content was about 3·5 mgm. per litre of melted ice. It is very remarkable that other concentrations could, within the limits of error, be written $3 \cdot 595 \times 2^p$, where p is a whole number, positive or negative. The highest and lowest concentrations were 56·33 and about 0·067 mgm. per litre respectively ; although the latter value is uncertain on account of the large experimental errors (amounting

¹ Hilding Köhler, *Über die Chlorverteilung und die Tropfengruppen im Nebel und über Farbenberechnung der Kränze im weissen Lichte nebst einigen kritischen Bemerkungen der Koagulationstheorien der Nebeltropfen*, *Arkiv för Matematik, Astronomi och Fysik*, K. Svenska Vetenskapsakademien, 24A, No. 9.

to 50 per cent.) at such low concentrations. On the presumption that all sea salts are present we get the concentration of these salts per litre of melted ice (according to Knudsen) on multiplication by 1.805.

H. Israël² has found almost the same proportion of chlorine in rain, viz., 3.42 mgm., and, thus, 3.42×2^2 . The fact that the concentration of chlorine in rain-drops diverges only very slightly from the concentration of the droplets in fogs and clouds, the mass of which is about a million times smaller, is of great importance.

Analyses of chlorine content in rain-water carried out over the period 1870-86 by Kinch,³ gave the following results:—

Average of 16 years, 3.81 mgm. per litre.

" " 12 " 3.36 mgm. per litre.

There is therefore no essential difference between the concentration of chlorine in the rain-drops and in the fogs on the level of the Haldde.

On the other hand, my own analyses on the Sonnblick, and similar analyses by Lipp and Lauscher on the Zugspitze and the Sonnblick,⁴ have shown that the concentration of chlorine in fogs decreases with the height. Rain generally falls from clouds lying at about the level of the Haldde (914 metres above sea-level). We shall explain later the reason of this decrease of the concentration of chlorine with the height above sea-level.

2. The measurements of the droplets gave an average size of $r = 8.86\mu$. According to theoretical investigations,¹ supported by the experimental observations of L. F. Richardson,⁵ a systematic error of, at most, 4 per cent. may attach to this value. Sometimes the size of the droplets changed unduly during a series of measures, and frequently the average value varied from series to series. When frequency curves were drawn for the series of measurements there were always, however, maxima at certain droplet sizes. The relation between those radii which gave these maxima could be expressed as $r = B \cdot 2^{n/3}\mu$ ($B = 8.82$), where n had whole (either, positive or negative) values. I therefore, for all separate measurements, calculated n also. This value (8.82) of B was obtained direct from the frequency curves. Frequency curves of n were drawn for all the measured series and from these it was clear that there is only one maximum, so long as the standard deviation of n is less than or equal to 0.19. With few exceptions these maxima were in the neighbourhood of values of whole numbers of n (or more exactly $n \pm 0.019 \pm 0.0050$). There further appeared such single series as $n \pm 0.426 \pm 0.0134$. Frequency curves with a greater standard deviation always showed maxima close to these values of n , although the radii of the droplets often varied from 3μ to 25μ .

I therefore made statistical examination, partly to examine the reality of these maxima, and partly to calculate more exactly the values of n . Thus this work was not carried out in order to prove any particular hypothesis. I have never made any hypothesis of the size distribution of the droplets. The separate measurements in the single series ($\sigma < 0.19$) grouped themselves round the average values of the whole numbers of n (or $n \pm 0.445 \pm 0.0070$) according to normal curves with $\sigma = 0.173$. This standard deviation is greater than that of the errors of measurement, which is on an average $\sigma = 0.053$ ($\sigma = 0.131$ for $n = 6$, to 0.029 for $n = -5$).

Hence it follows that the size of droplets present in preponderating proportions in the clouds changes, and that other sizes are found than those which give the maximal frequency.

Series including 2 to 4 maxima were also statistically worked out, and it was found that even these gave normal curves. We then calculated A_3 (the measurements grouped round the whole n , which we now call the

² *Bioklimatische Beiblätter*, Heft. 2, 1934.

³ *J. Chem. Soc.*, 1887, 92.

⁴ *Jahresberichte der Sonnblickvereins*, 1931 and 1933.

⁵ "The Brown Corona and the Diameter of Particles," *Quart. J. Roy. Meteor Soc.*, 1925, 51, 1.

3-group), and A_1 (the measurements round $n + 0.445$, which we now call the 2-group). The figures for n and σ and the relative number A , expressed as a percentage of the number of measurements, were :—

<i>The 3-group.</i>	<i>The 2-group.</i>
$n : n + 0.018 \pm 0.0053$	$n + 0.452 \pm 0.0081$
$A : 62.7$ per cent.	37.3 per cent.
$\sigma :$	0.177 for both groups.

From all these measurements (which contained series with up to 15 maxima), we calculated by another method the percentage distribution, viz. :—

<i>The 3-group.</i>	<i>The 2-group.</i>
60.4 per cent.	39.6 per cent.

The distribution of the series earlier calculated being :—

<i>The 3-group.</i>	<i>The 2-group.</i>
61.9 per cent.	38.1 per cent.

The two being in unexpectedly good accordance.

If the masses of the droplets was then calculated, it was found that these could be written in the proportions $2 : 3 : 4 : 6 : 8 : 12 : 16$ and so on.

In this mass series, 2×2^n corresponds to the droplets in the 2-group and 3×2^n to the droplets in the 3-group. It has later been found that two other groups probably exist, corresponding to the figures 5 and 7 in the above-mentioned mass-series. The complete series can, then, be written : $2 : 3 : 4 : 5 : 6 : 7 : 8 : 10 : 12 : 14 : 16$ and so on.

These results are empirical and valid for mountain fogs and clouds ; if they are wrong there must be some unknown error in the method of measurement. Recently Niederdorfer ⁶ has found in rain, by quite another method, the same mass distribution as is given in the above-mentioned series. The results obtained by Findeisen ⁷ and Hageman ⁸ are valid for lowland fogs and are obtained through measurements of separate droplets. This method of measurement, which (in regard to droplets in fogs and clouds) has been previously compared with the optical method of measurement, cannot be compared in regard to reliability.

I cannot yet offer any explanation of the classification of the groups of droplets and quantity of chlorine. It has, however, been necessary to give an account of these facts in order to make this description comprehensible.

The Thermodynamics of the Condensation on Hygroscopic Nuclei.

Taking the average values of 3.595 mgm./l. chlorine and radius of droplets 8.86μ , we proceed, as in a previous paper, ⁹ where r was taken as 8.82μ . On the supposition that all sea-salts are present in the nucleus, it is calculated that a nucleus of dry sea-salts has the mass of 1.847×10^{-14} gm. I here take 10^{-14} gm. as mass unit and make $\alpha_1^3 = 1.847$. As the quantities of chlorine in the frost are distributed in the proportion 2^n , the masses of the nuclei must also stand in the same relation.

Instead of r I here use n as a variable which varies continually. If $8.82 \mu = 8.82 \times 10^{-4}$ cm. $= B$, we then get $r = B \cdot 2^{n/3}$.

⁶ *Met. Z.*, 1932, 49, 1.

⁷ *Gerl. Beitr.*, 1932, 35.

⁸ *Ibid.*, 1936, 46.

⁹ Hilding Köhler, *Zur Thermodynamik der Kondensation an hygroscopischen Kernen und Bemerkungen über Zusammenfliessen der Tropfen*, *Meddelande från Statens Meteorologisk-Hydrografiska Anstalt*, 3, No. 8, Stockholm, 1926.

From this it follows that $p - n = L$ determines the concentration of the droplet. At a certain value of L the concentration is invariably independent of p and n . Table I gives concentrations expressed in gm. of salt per 1000 gm. of solution at different values of L .

TABLE I.

$p - n = L$	Concentration gm. per 1'000 gm.
17	529.3
16	326.3
15	184.6
14	98.8
13	51.2
12	26.1
11	13.2
10	6.61
9	3.31
8	1.66
7	0.831
6	Then halve
5	
4	
3	
2	

The total quantity of water in a liquid state in the weight unit of air depends, not only on the concentration of the droplets, but also on the number of nuclei, if every nucleus becomes the centre of a droplet. This number N is of great importance for the understanding of atmospheric condensations.

We now calculate, in terms of the whole quantity of salt being NaCl (since the chemical constants of this salt are well known), and on the supposition that the same laws apply to the small volumes, with which we are dealing, as apply for larger volumes. Now, a salt in water lowers the vapour-tension, but the latter is higher above a convex than above a plane surface. The specific volume v' of a droplet with the radius $B \cdot 2^{n/3}$ and with salt nucleus can be written

$$v' = \frac{1}{1 + \alpha_1^3 \cdot \delta^3 \cdot 2^{p-n}},$$

where δ^3 is a constant, equal to 2.483×10^{-6} . If NaCl has a constant dissociation of 75 per cent., the vapour tension e_i above a plane solution surface can be expressed as:—

$$e_i = e_m \frac{1 - \epsilon_a \cdot \alpha_1^3 \cdot 2^{p-n}}{1 - \epsilon_i \cdot \alpha_1^3 \cdot 2^{p-n}},$$

where $\epsilon_a = 9.930 \times 10^{-7}$, $\epsilon_i = 1.149 \times 10^{-6}$, and e_m the pressure of a saturated vapour.

The vapour tension above a droplet of radius $r = B \cdot 2^{n/3}$ of this solution is:

$$\log e = \log e_i + \frac{2 \cdot s \cdot v'}{R_1 \cdot T \cdot B \cdot 2^{n/3}},$$

where R_1 is equal to the gas constant of the water-vapour (4706.91),

T is the absolute temperature, and

s is the capillarity constant, which is a function of temperature and concentration as follows:—

$$s = s_0(1 - bT) + \frac{c \cdot \alpha_1^3 \cdot 2^{p-n}}{1 - \beta^3 \cdot \alpha_1^3 \cdot 2^{p-n}},$$

where $s_0 = 1.1683 \times 10^{-1}$,

$b = 1.2518 \times 10^{-3}$,

$c = 8.4 \times 10^{-8}$,

$\beta^3 = 9.960 \times 10^{-7}$.

In order that a droplet of solution shall remain unchanged in the atmosphere, the vapour tension above it must be equal to the pressure of the vapour in the atmosphere. In Fig. 1 the vapour tension above

droplets at different values of α^3 at different concentrations is shown for $T = 273$. It will be seen that the vapour tension first increases with decreasing concentration, passes a maximum and approaches asymptotically the pressure of the saturated vapour. The maxima of the vapour tension become more and more pronounced the smaller α^3 is. If many unequally large nuclei appear in the atmosphere, it follows that on condensation a selection must take place so that, at first, droplets which have been formed on the larger nuclei pass maxima, at which moment droplets on smaller nuclei must evaporate until their vapour tension balances those droplets which have been formed on the larger nuclei. This theoretical result corresponds wholly to the fact that the concentration of Cl in the droplets decreases with the height, as shown by Lauscher and Lipp.⁴

If the sum of the vapour and water absorbed by the hygroscopic nucleus is K , the solution droplets must have a vapour tension equal to the vapour pressure prevailing in the air; the quantity of vapour x is calculated from

$$x = K - M \cdot 2^n (1 + \alpha_1^3 \cdot \delta^3 \cdot 2^{-pn}),$$

where

$$M = N \cdot \frac{4}{3} \cdot \pi (8.82)^3 \times 10^{-12}$$

and N = the number of droplets in 1 gm. of air condensed on the nucleus, $\alpha_1^3 \cdot 2^p$ and δ^3 have the same values as before. N is very large; the larger it is the more quickly x approaches zero.

The latent heat of condensation λ for the solution droplets can easily be calculated:

$$\lambda = AT \left[R_1 T \frac{\partial \log e}{\partial T} + \frac{\partial e}{\partial T} \cdot \frac{\partial v'}{\partial x} (K - x) - R_1 x \frac{\partial \log e}{\partial x} \right],$$

where A is Joule's equivalent. The middle term in the brackets can be neglected in comparison with the others. From Clapeyron's formula for the latent heat of evaporation of water,

$$\lambda_0 = A \cdot R_1 T^2 \frac{\partial \log e}{\partial T},$$

we get:—

$$\lambda = \lambda_0 + \frac{2 \cdot A \cdot T^2 \cdot v'}{B \cdot 2^{n/3}} \cdot \frac{\partial}{\partial T} \left(\frac{s}{T} \right) - A \cdot R_1 \cdot T \cdot x \frac{\partial \log e}{\partial x}.$$

In this expression the second term is always negative. The third term is negative, if e increases with decreasing x , which is the case before the maximum of vapour tension has been reached (see Fig. 1); this term is greater than the second, so that within this interval

$$\lambda > \lambda_0.$$

After the maximum has been reached, the third term is positive but, since the second term is always negative, it follows that within this interval

$$\lambda < \lambda_0.$$

Without detailing the calculations we can now see how far the droplets increase on nuclei (which we regard as droplets of a more or less concentrated solution of salt) if a quantity of air is adiabatically cooled.

If a quantity of heat q is added to the system of droplets-water-vapour, this heat is used partly in heating the system and partly in evaporation of droplets, according to the formula

$$q = CdT + \lambda dx.$$

When the entropy is a whole differential we get

$$C = T \int \frac{\partial}{\partial T} \left(\frac{\lambda}{T} \right) dx + F(T),$$

where $F(T) = K$ or the whole quantity of water of the system, so long as the specific heat of water is regarded as independent of the temperature and equal to unity.

We write the change of entropy

$$\int \frac{q}{T} = \int \frac{C}{T} dT + \int \frac{\lambda}{T} dx + \text{const.} = S(nT) + \text{const.}$$

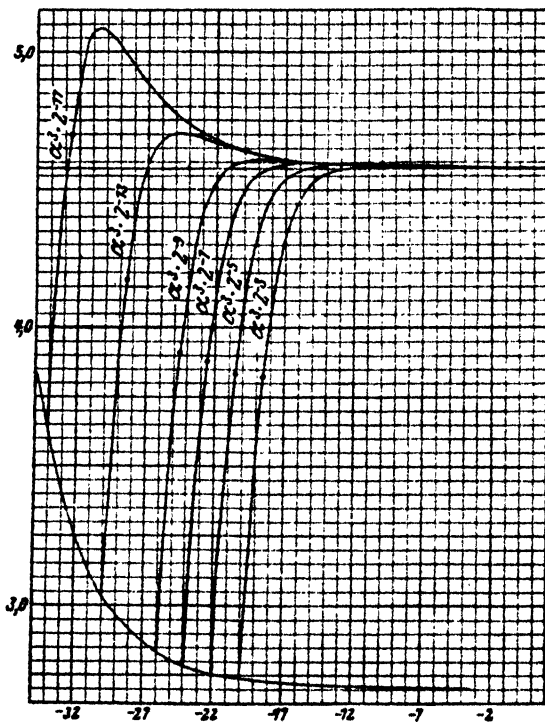


Fig. 1.

If these processes take place in the atmosphere, the corresponding expression for the changes in the air must be added to this equation :—

$$\int \frac{q}{T} = c_p \log T - AR \log (P - e) + \text{const.}$$

where P = total atmosphere pressure and c_p = specific heat of dry air at constant pressure.

Treating the laws of Boyle-Mariotte-Gay Lussacs as valid for both water-vapour and air we get, if the specific volume of the air is v_1 :—

$$P = \frac{RT}{v_1} - e; \quad e = x \cdot \frac{R_1 T}{v_1}$$

from which it follows :—

$$\log (P - e) = \log \frac{R}{R_1} + \log e - \log x.$$

Through the setting-up and combination of the two systems we get finally :—

$$\int \frac{q}{T} = S(nT) + c_p \log T - AR \log e - AR \log \frac{R}{R_1} - AR \log x + \text{const.},$$

where e is both the partial pressure of water-vapour in the air and the vapour tension of the droplets. The variation of e_m with temperature is obtained according to the formula :—

$$e_m = 60.49228 - \frac{7027.20766}{T} - 5.8691014 \log T.$$

If the system works under adiabatic conditions $\int \frac{q}{T} = 0$. The constant is determined by the initial conditions. The value of N , which states the number of particles per gm. of dry air is of great importance

to the calculations, as also is the choice of α^3 . We have chosen N in the following way : N_1 is the number of particles if $\alpha^3 = \alpha_1^3$. Then, $N = N_1 \times 2^p$ if $\alpha^3 = \alpha_1^3 \times 2^{-p}$ and $N_1 = 2 \times 10^6$ corresponds to 258.6 nuclei per c.c. of air, a very small number which may be increased a hundred or a thousand-fold. The first fundamental question may be formulated as follows: Why is the number of droplets in fogs so much smaller than the number often measured with Aitkens' Nucleus Counter ?

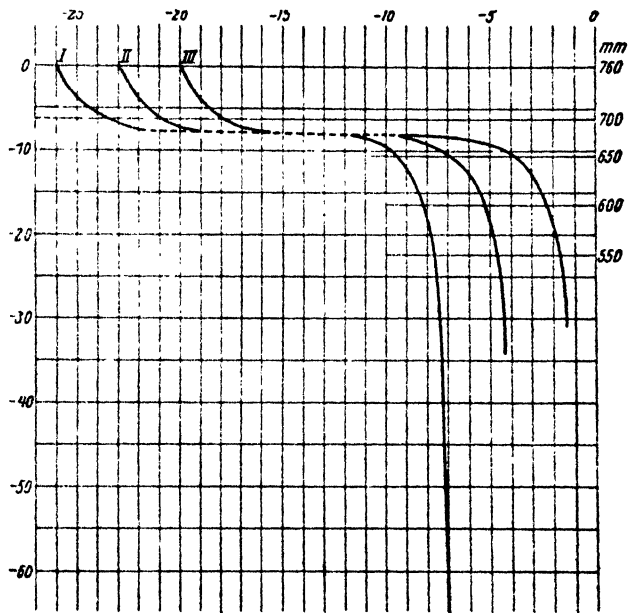


FIG. 2.

I : $\alpha^3 = \alpha_1^3 \cdot 2^{-9}$	$N = 10^5 \cdot 2^{10}$ per gm. of air
II : $\alpha^3 = \alpha_1^3 \cdot 2^{-4}$	$N = 10^5 \cdot 2^7$ " " " "
III : $\alpha^3 = \alpha_1^3 \cdot 2^{-3}$	$N = 10^5 \cdot 2^4$ " " " "

Fig. 2 shows how the droplets increase (assuming continued condensation) if the initial concentration is expressed by $p - n = 17$, and N has the values shown, the initial temperature being 273 and $P - e$ being initially 760 mm. The first part of the curve is uncertain as not all the NaCl is dissolved until at about $p - n = 15.3$. Thus for $p = -3$, $n = -18.3$. The increase is shown in Fig. 3 for the initial temperature $T = 283$. In both figures n is abscissa and $T - 273$ ordinate, and the atmospheric pressures are also shown.

It will be seen that the increase occurs very rapidly after that the maximal vapour-pressure has been reached. Further, the size of droplets at a certain temperature decreases with N . We cannot see so clearly that, after having reached a certain size, the size of the droplets can

no longer be doubled through continued condensation. We have referred to the last value of n , which is obtained through continued condensation as "the last whole n ." This value varies with N . The greater N is, the smaller the whole n becomes.

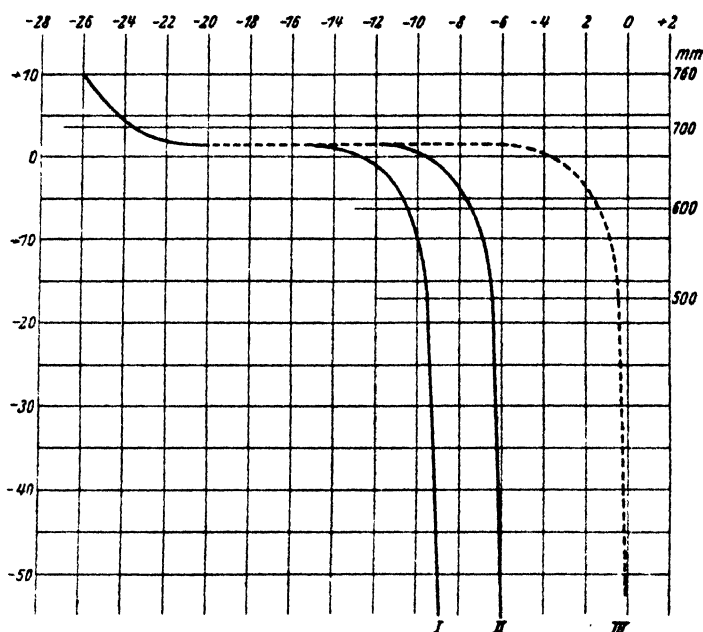


FIG. 3.

$$a^2 = a_1^2 \cdot 2^{-8}$$

I: $N = 8 \cdot 10^8$ II: $N = 10^8$ III: $N = 10^8 \cdot 2^{-4}$ per gm. of air.

TABLE II.

N ($\times 10^8$)	$a^2 = a_1^2 \cdot 2^{-8}$			$a^2 = a_1^2 \cdot 2^{-6}$			$a^2 = a_1^2 \cdot 2^{-4}$			$a^2 = a_1^2$		
	The last whole n .	Concentration of Cl. (gm./l.).	Final Temperature.	The last whole n .	Concentration of Cl. (gm./l.).	Final Temperature.	The last whole n .	Concentration of Cl. (gm./l.).	Final Temperature.	The last whole n .	Concentration of Cl. (gm./l.).	Final Temperature.
2										+1	1.798	253.7
8										-1	7.190	253.7
16							-2	1.798	253.9	-2	14.38	253.7
64							-4	7.190	253.9			
128				-5	1.798	254.2	-5	14.38	253.9			
512				-7	7.190	254.2						
1024	-7	0.899	211.0	-8	14.38	254.2						
4096	-9	3.595	211.0									
8192	-10	7.190	211.0									

In Table II are expressed the values of the last whole n , the concentration of chlorine in these droplets and the temperature T which this n reaches if the initial temperature is 273 and the initial concentration can be expressed by $p - n = 17$. From this table it follows:—

1. If $\alpha^3 = \alpha_1^3$ the droplets can, through condensation, change to $n = +1$, corresponding to $r = 11.11 \mu$ if the number of nuclei N per gm. of dry air is 2×10^5 , corresponding to the low number of 258 per c.c. of air at 0° and 760 mm. Through want of vapour the mass of the droplet cannot later on be doubled. If the number of nuclei is 16×10^5 per gm. of dry air or 1064 per c.c., the last whole n cannot on the same nucleus exceed -2 , corresponding to $r = 5.56 \mu$. On increasing N the greatest whole n decreases, as is seen, to very small figures.

2. *The concentration of chlorine at these last whole n is that which has in fact been obtained on analysis of hoar-frost.*

3. The greater N is, the more the air must be cooled before the last whole n is reached, the higher the air thus must rise, before this n is reached; thus the concentrations of chlorine due to condensation we have found are reached.

4. The greater N is, the higher the concentration of chlorine is, when the last whole n is reached. At a certain value of N the concentration decreases with α^3 , but the last whole n remains the same for different α^3 , as long as N is the same. If the initial temperature T is 283, the last whole n is only one unit greater. There is no essential difference in the results obtained, if the initial temperature is varied.

It follows that these solution-droplets, if accompanied by a rising quantity of air, cannot reach the size of raindrops, the masses of which are one or several million times larger than the droplets corresponding to the last whole n calculated here.

Moreover, the concentration of chlorine in raindrops is the same as in the droplets in fogs and clouds, which are millions of times smaller. From this it follows that raindrops never arise from condensation of the droplets in fogs and clouds; if this were the case the concentration of chlorine must of course be enormously small, on the assumption that chlorine salts are nuclei. Even the droplets in fogs and clouds cannot be obtained through direct condensation, since the concentration of chlorine is independent of the size of the droplets. *The increase must take place so that the concentration remains constant.*

From the circumstance that droplets, formed on different α^3 at different vapour tensions and sizes, pass the maximal vapour tension, it follows that at first larger nuclei come into action and then smaller and smaller. A selection of nuclei takes place. In consequence of this and of the results found in the table, the concentration of chlorine must decrease with the height above sea-level. This has been confirmed by the analyses of Lauscher and Lipp. We conclude finally that the number of droplets in fogs and clouds is much smaller than the number of nuclei obtained in Aitkens' Nucleus Counter. This also points to the fact that increase in dimensions of droplets of any particular size must take place otherwise than through direct condensation. Their size must be independent of the concentration. This increase in number perhaps causes that distribution of groups, of which we have spoken above.

THE NATURE OF THE DISPERSOIDS IN COUNTRY AND TOWN AIR.

By J. H. COSTE.

Received 13th March, 1935.

If the atmosphere consisted only of the mixture of gases known as air, conditions on this planet would be very different from what they now are. The characteristics of the air as we know it are largely determined by the very small proportion of solids and liquids which form vast, or merely large disperse systems, in it.

Of these disperse systems some are natural and of meteorological significance, whilst others which may or may not be of similar significance are the result of human activities, which they, in turn, may greatly affect. The former class are mainly systems in which water is the major constituent of the disperse phase, whilst the latter are more varied in character. The great dilution of most of these systems, together with the low density and viscosity of the medium, makes investigation difficult, and the systems themselves unstable. The most obvious visual means of investigation have given us classification of clouds, based on Luke Howard's nomenclature, an international scale of visibility and various more or less satisfactory methods of gauging smoke density for the purpose of administering very difficult Acts of Parliament.

Ions and Nuclei.

The study of the conduction of electricity through gases has shown that charges are carried by (a) "small ions" which behave as if they were aggregates of up to 30 molecules (of something) carrying one electronic charge, and by (b) "large" or Langevin ions, similarly charged, but consisting of about a million molecules. The radius of small ions varies from about 3 to 10×10^{-8} cm. and of the Langevin ions from 10^{-6} to 10^{-5} cm., but there is no sharp division, it appears probable that large ions are Aitken nuclei (c) which have captured small ions and thereby become charged. Aitken nuclei, whether charged or uncharged, have a mean radius something under 5×10^{-6} cm.

J. J. Nolan and P. J. Nolan¹ have described a new method of counting small ions which, they claim, yields results with ease and accuracy. Large ions can be determined by differential counts with Aitken's counter, with and without a condenser to remove charged nuclei (ions). Scrase² has recently investigated the Aitken counter, in which the number of hygroscopic nuclei is determined by counting the drops falling on a graticule after the adiabatic expansion of a determined volume of air saturated with water vapour. Aitken³ at first (1879) believed that the hygroscopic nuclei thus counted were dust particles, and continued to call them so after he had realised that they were droplets of unknown

¹ J. J. Nolan and P. J. Nolan, *Proc. Roy. Irish Acad.*, 1935, 42A, 15-19.

² F. J. Scrase, *Quart. J. Roy. Met. Soc.*, 61, 367-79.

³ J. Aitken, *Coll. Sci. Papers*, 1923, 34-74.

composition. On this point, M. G. Bennett⁴ says "As to the source of the nuclei, there are two obvious possibilities—the sea and chimneys. No doubt the sea provides most of the nuclei operative in genuine sea fogs, and chimneys are able to provide all the nuclei required for town fogs; but the main source of such nuclei in country air is still a matter under discussion. . . ." N. Fuchs⁵ also refers to the lack of knowledge of the nature of large ions:—"Die einzigen bisher untersuchten amikroskopischen Aerosole waren die sogenannten Langevinschen Ionen, d.h. geladene Teilchen von ganz unbestimmter Natur." There is undoubtedly much evidence supporting the view that many of the nuclei found in air everywhere are the result of the evaporation of droplets of sea water projected into it by breaking waves and whirled over the earth by the action of winds. I have repeatedly found chlorions in water condensed from London air and, although these may in part have resulted from the volatilisation of the chlorine often found in some form (not, apparently, invariably, as chlorides) in coal, the sea seems a more prolific source. Rain water, each drop of which had its origin in a nucleus, seems invariably to contain chlorions,⁶ as does river water, even in upland and mountainous districts. The water of rivers fed by tropical rains,⁷ which usually fall in larger drops than in temperate climates, contains a less concentration of chlorions than that of European rivers,⁸ where small raindrops may be considered as more concentrated solutions. The chlorion content of the Thames⁹ (before it is contaminated with sewage, which raises the chlorion concentration) is of the order to be expected from the composition of the rainfall and subsequent evaporation. Further, Köhler⁹ has analysed the saline content of both clouds and rime (derivatives of nuclei) in the Arctic circle, and based a theory of condensation on the contents of chlorides.

An argument for this theory can be based on the better agreement of the chlorion contents of the rain collected in two deposit gauges a few yards apart at Kew Observatory, as compared with other solid constituents, but this does not necessarily mean that the halogen is derived solely from the sea, since it is probable that the chlorine content of fuel may account for great part of it. In some tentative experiments I have not so far been able to detect bromine, which constitutes about 0.5 per cent. of the halogen content of sea water, in the Kew deposits.

H. L. Wright and I¹⁰ have investigated the artificial formation of nuclei by burning various fuels (e.g. pure alcohol) in an enclosed atmosphere freed from pre-existent nuclei and from sulphur dioxide and other acid gases, and by the electrical heating of metal (e.g. platinum) surfaces, and found that formation of nuclei occurred. Of the hypotheses which may be advanced in explanation, the only one which appears to cover all the facts is that droplets of nitrous acid are formed from constituents of the air under suitable conditions of temperature, since this was detected and many nuclei found in the atmosphere after the experiments; nitrous acid was also found in the condensates. Fuming sulphuric

⁴ M. G. Bennett, *Quart. J. Roy. Met. Soc.*, **60**, No. 253, "Some Problems of Meteorology," 114-25.

⁵ N. Fuchs, *Acta Physicochimica U.R.S.S.*, **3**, 1935, 61-78.

⁶ "The Investigation of Atmospheric Pollution," *D.S.I.R. Annual Reports*.

⁷ C. M. Tidy, *J. Chem. Soc.*, **37**, 274.

⁸ *Reports of Director of Water Examinations, Met. Water Board*.

⁹ H. Köhler, *Gerl. Beil. Geophys.*, 1931, **29**, 168-86.

¹⁰ J. H. Coste and H. L. Wright, *Phil. Mag.*, **7**, 20, 209-34.

acid and sea water were found to be active producers of nuclei when sprayed into air, whilst other liquids were relatively feeble producers of nuclei. G. B. Courtier and I¹¹ have also found sulphuric acid in the condensate from London air which had been freed from sulphur dioxide. We therefore believe that although sea water is the chief constituent of nuclei in nature, most of the nuclei produced in civilised countries by the fires, furnaces, etc., associated with human activity are droplets of nitrous acid, some sulphuric acid probably being formed also. The formation of sulphuric acid in air containing sulphur dioxide gas with nitrous acid, partly in the gaseous phase and partly in droplets seems inevitable, but a study of sulphuric acid dispersoids in air by N. Fuchs⁸ shows that combination occurs easily between droplets, so that a limiting concentration is easily reached beyond which the aerosol becomes unstable, and deposition on surfaces (leading probably to corrosion if they are metallic) occurs. Whether this is the correct, or at least a partial explanation, is difficult to say, but the concentration of sulphuric acid is very small, of the order of 1 per cent. of that of sulphur dioxide, in air.

Further work with Wright* has shown that nuclei in London air may contain the nitric and ammonium ions, as well as those already mentioned. In each case the ions identified were found in condensates from air freed from sulphur dioxide. The known properties of solutions show that any soluble and hygroscopic substance in moist air is likely to yield Aitken nuclei, although at lower tensions of water vapour some solutes will be more effective as drop-formers than others.

The concentration of nuclei in air varies very greatly, but the number per c.c. is generally much less in country air than in that of towns. The concentration over the sea is also usually low. A few figures from various sources will show this, Table I. :—

TABLE I.

Observer.	Place.	Number of Nuclei/c.c.
Aitken.	Top of Rigi.	210 to 3,450.
"	Cannes.	1,550 to 150,000.
"	Mentone	1,200 to 5,000.
"	Lucerne.	616 to 23,000.
"	Kingairloch.	205 to 3,100.
"	Ben Nevis	335 to 473.
"	Garelochhead.	16 to 7,600.
Rankin (quoted by Aitken).	Ben Nevis.	7 (not unusual).
Aitken.	London (garden).	48,000.
"	" (Victoria Street).	150,000.
"	Paris (streets).	92,000 to 260,000.
Thellier.	"	3,500 to 260,000 (average 62,500).
Coste and Wright. 1935-36.	London (County Hall).	23,000 to 200,000.
	" "	

Wright¹² (Fig. 1) has found a small seasonal variation in the number of nuclei in the air at Kew, the minimum occurring in the summer

¹¹ J. H. Coste and G. B. Courtier, Paper No. 23.

* *Unpublished.*

¹² H. L. Wright, *Quart. J. Roy. Met. Soc.*, 1935, 61, 71-80; and *Geophys. Mem.*, No. 57.

months June to August. He also found a distinct decrease as the day advanced from nine hours to fifteen hours. Mm. Thellier in Paris¹³ also found nuclei "*beaucoup moins nombreuses l'après-midi que le matin*," but observed no marked seasonal variation.

Aitken¹⁴ pointed out that what he called "purifying areas" existed "where most clouds are formed and most rain falls." In four of these areas he found in the years 1889 to 1893 the lowest number of "particles" in the air coming from

Mediterranean.	Alps.	Highlands (of Scotland).	Atlantic.
891	381	141	72
the averages for these localities being			
1611	892	552	338

Over the narrow English Channel (presumably between Calais and Dover) he found 7000, but Bennett states that "the numbers of large ions and Aitken nuclei at sea (about 200 per c.c.) are very much less than over land."

The mean mass of a nucleus is less than 1×10^{-15} gm. J. J. Nolan and V. H. Guerrini¹⁵ have recently found that the radius of the nuclei in Dublin air is 2.85×10^{-6} cm. and their mass 1.68×10^{-16} gm. The mass of the nuclear content of the air, even when the number is up to 10^6 /c.c., is of the order of 10^{-5} of the water content of saturated air.

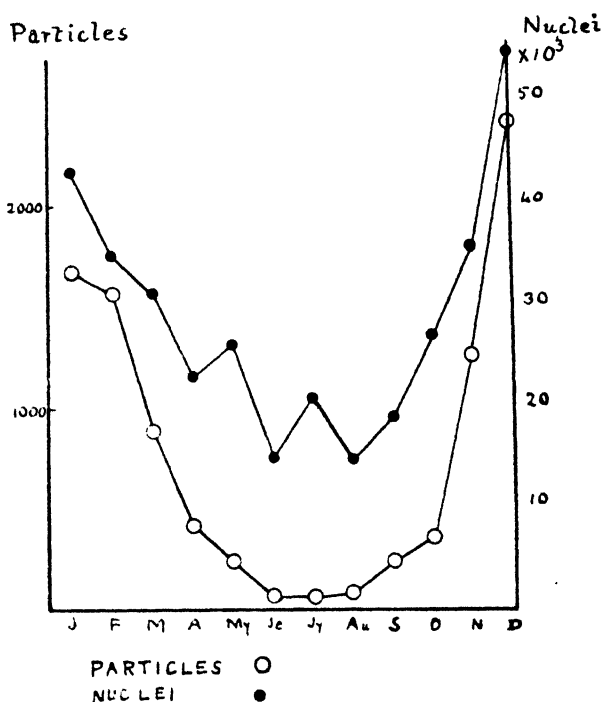


FIG. 1.—Seasonal variation of dust particles and nuclei at Kew, 1928-30 (Wright).

Fog and Cloud are derivatives of nuclei, formed by condensation on them of water vapour. M. G. Bennett⁴ gives the limits of radius of fog droplets as from 4×10^{-4} cm. to 3×10^{-3} cm., with velocity of falling from 0.2 to 11 cm./sec. and of cloud drops an upper limit of 1×10^{-2} with a velocity of falling of 121 cm./sec. remarking "it is seen that a small fog droplet falls so slowly that it may be regarded as almost permanently suspended, and even in the case of a large drop, a current

¹³ O. Thellier, *Comp. Rend.*, 201, 248-50.

¹⁴ J. Aitken, *Coll. Sci. Papers*, 397-9.

¹⁵ J. J. Nolan and V. Guerrini, *Proc. Roy. Irish. Acad.*, 1935, 43A, 2.5-24.

of air rising with quite a reasonable velocity would be sufficient to maintain it at a constant height."

When air contains, besides natural dispersoids, tarry or sooty particles, coalescence occurs to a greater or less extent and, since fog is usually associated with still air conditions, the concentration of smoky particles becomes very high and the fog assumes the yellow to black hue well known to dwellers in large towns. Since most fuel contains sulphur, the concentration of sulphur dioxide and to a less extent of sulphuric acid becomes high, and the fog is irritant as well as dark. The variation of sulphur dioxide and black suspensoids during the fog of 23rd December, 1935, in London, is shown for part of the day in Fig. 2. With a temperature inversion over and around a large city the combined

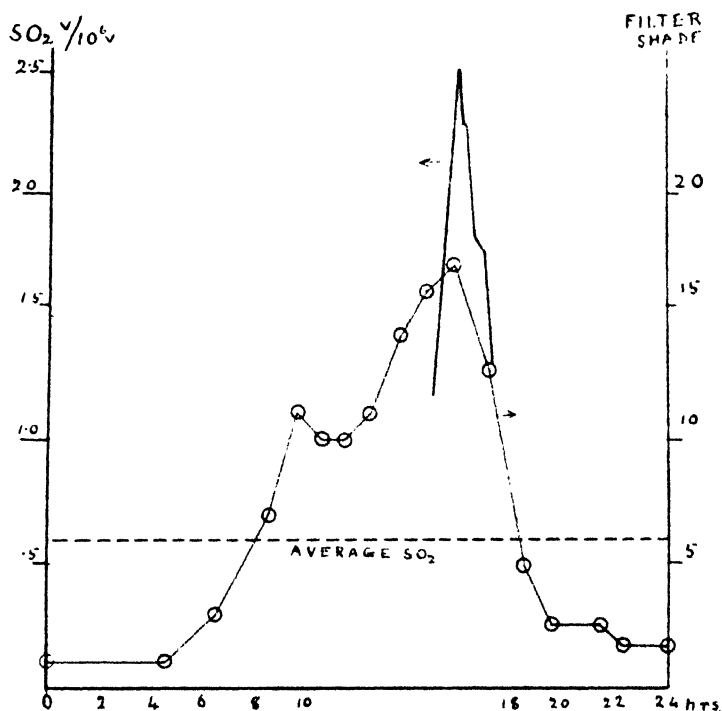


FIG. 2.—Owen's filter shade and SO_2 at County Hall, London, during foggy day, 23rd December, 1935.

result of this and the heating effect of many warmed buildings may cause an overhead fog with darkness but reasonable clarity in horizontal directions. Professor Firket will speak on the effect of such a sulphurous fog in the Meuse valley.

Rain Drops as the ultimate derivatives of nuclei, may reach a radius of about 0.27 cm. (approximately the maximum calculated from the surface tension of water against air), and fall through air with a terminal velocity of about 800 cm./sec. Even such a large drop must spend a considerable number of seconds in falling from a cloud to the surface of the earth, and smaller drops spend much longer. During its fall, a drop is likely to become associated with other dispersoids in the air, and Dr. F. J. W. Whipple and I have found* that rain water collected

* Unpublished.

in a clean vessel contains appreciable amounts of salts and of insoluble matters. Some portion of the salts is accounted for by the hygroscopic nuclei on which drops form, but insoluble matters can only be derived from suspensoids in the air. The fact that considerable amounts of soluble and insoluble solids are found in water collected in deposit gauges used for investigation of atmospheric impurity⁶ can hardly be adduced as proof that rain itself actually contains other non-aqueous matter than is derived from nuclei, since some may have been washed from dust falling into the gauges in dry periods, but all the matter collected in these gauges is derived from dispersoids in the air, and it may amount during a month to kilogrammes per square dekametre.

The nature of this solid matter (some of which is undoubtedly proper to the nuclei) is investigated, in a limited way, under the scheme of the Atmospheric Pollution Committee, the deposits of soluble and insoluble matter being determined and separated into tar, carbonaceous matter other than tar, sulphates, chlorides and ammonia. I have found on microscopical examination of the insoluble matter collected in London deposit gauges: spheres of fused matter—some glassy with gaseous inclusions, some opaque and light coloured with a warty surface, as if bubbles of gas had reached the periphery and burst as the mass solidified, some of magnetic iron oxide, others of coke, sintered sausage-shaped particles also evidently formed at a high temperature, coal, charred wood, textile fibres, plant hairs and other vegetable tissues, sand mostly from quartz, less often from flint, and occasionally scales of lepidoptera.

The Finer Solid Dispersoids of Air can be determined with reasonable accuracy by dust counters of which the Owens jet instrument⁶ and the thermal precipitation instrument designed by Whytlaw Gray and Green⁶ are the most efficient, or by Owens' air filter,⁶ which is applicable only for black (soot) particles, in which the stain on paper through which a known volume (usually 2 litres) of air has been filtered, is compared with the stain produced by a known mass of carbon. An interesting investigation was carried out by H. G. I. Robins in the country around Norwich, and the results were discussed by Professor David Brunt,¹⁶ who found (*inter alia*) that "the pollution is greatest in winter, least in summer, and intermediate (and equal) in spring and autumn," and "reaches an approximately steady value, showing no further diminution, at a distance estimated at 4 miles in spring, 5 miles in summer and autumn and 6 to 7 miles in winter." Brunt also concluded "that the cloud is effectively 4 or 5 miles wide at 3 miles from the city. As it is at least 2 miles wide initially, this result is not surprising."

The quantity of dispersed matter collected on the cover glass of a dust counter or the paper of an air filter is too small for ordinary microchemical analysis, but I have *qualitatively* examined stains filtered on ashless paper from several cubic feet of air in the manner suggested by G. M. B. Dobson.

Calcium carbonate and sulphate were found, in addition to soot and tar, in stains obtained by Dobson at Oxford, and kindly placed at my disposal; no free acid was found by him when the stains were fresh, but the presence of calcium carbonate and sulphate accounts for this, as calcium carbonate is likely to be present in air in amount enough to neutralise any acid droplets which come in contact with it, and which are most probably present, though, as Courtier and I show in another paper, only in very small amount.

¹⁶ D. Brunt, *The Invest. Atmo. Poll, 17th Report*, 50-58.

Living Matters.

An interesting and important group of suspensoids found in air comprises living and dead organisms and organic structures. Bacteria, moulds (spores), spores of ferns, pollen grains and infusoria in the loricated state may fairly be considered as dispersoids, but it would hardly be legitimate to include seeds with pappi or winged animals.

Bacteria and moulds in air have been investigated by many workers, but the subject has received no systematic attention. My colleague, Dr. J. Graham Forbes, F.R.C.P., examined the bacterial and hyphomycete content of the air of the London tube railways,¹⁷ and with the exception of one or two pathogenic species of *aspergillus* among the moulds, no definitely pathogenic organisms were identified out of the large number of colonies examined. W. F. Wells has studied air borne infection.¹⁸

Interesting proof of the distribution of fern spores in air can be seen in the growth of ferns in the neighbourhood of the electric light bulbs lighting the Cheddar caves and Kent's Cavern at Torquay. I found an interesting case of air-borne vegetable suspensoids at Arcachon. The streets were strewn, in places where dust could collect, with a bright yellow, sulphur-like powder; it was also on the sands of the seashore. Examined microscopically, it was indistinguishable from the pollen of *pinus maritima*, grown in the forests along the Basque coast for the production of turpentine. The appearance of growths of *protococcus viridis* and, rarely, of the red variety *haemococcus* in any stagnant water, whether in a waterbottle or a roadside puddle, and on the bark of trees is evidence of its widespread occurrence in air, and of the readiness with which it will settle out under quiet conditions.

Hygroscopic nuclei and the finer dispersoids, sooty or otherwise, are found in greater quantity in town than in country air. This is only to be expected, since the higher numbers are always associated with fire, which is a relatively rare phenomenon in nature. An exception should, perhaps, be made of volcanic districts, but I have found no observations on this point, except the ascription of various phenomena to the dust projected into the air in the Krakatoa eruption. The few specimens of Krakatoa dust which I have seen were very coarse, and could not have remained in the air for long.

The relatively large vegetable suspensoids may mostly be derived from country sources, but few observations of atmospheric impurity have, it seems, been made on country air, compared with the large number on town air. I hope in the near future to be able to work on country air. It may, however, be remarked that the leaves of plants in towns are usually covered with dust (largely of the kind associated with chimneys), whilst leaves in the country (now that our roads are no longer dusty), are seldom obviously dusty.

Characteristic Town Suspensoids, above the dimensions of nuclei and soot or dust-counter particles (from, say, 1 to 1000 μ) mostly result from combustion of solid fuel, and consist of silicates (if from industrial furnaces usually spheres, showing complete fusion of the fuel ash, or sintered particles) with particles having the characteristic foam structure of coke and sometimes covered with minute spheres of ash.* Ash from

¹⁷ J. Graham Forbes, *J. Hyg.*, 1924, 22.

¹⁸ W. F. Wells, *et al. Amer. J. Hyg.*, 1934, 20, 611-18; *ibid.*, 619-27.

* If combustion had gone on further, they would either have coalesced or become free spheres; domestic fires, on the other hand, where the temperature is lower, yield a flaky or shaly ash.

pulverised fuel furnaces, usually consists of spheres which are often hollow, or at least contain gas inclusions, although long sintered particles are sometimes seen. This hollow form causes them to have a lower apparent density than would be expected of silicates,²⁰ but grinding in an agate mortar will bring up the density and show "postage stamp fractures" where bubbles of gas have been broken. It is rather remarkable that pulverised fuel ash often contains a very appreciable proportion of unburnt coke. Another characteristic constituent of ash from high temperature furnaces is magnetic oxide of iron in spheres or sintered fragments; they contain ferrous and ferric iron, and are readily magnetised. That this has been fused indicates a temperature of about 1600° C.

Some notion of the nature of the coarser dispersoids falling through the air can be gathered from examination of the insoluble matter collected in the standard deposit gauges. Those in the London parks collect spheres, indicating industrial pollution, with coke and amorphous or laminar "ash," probably from domestic grates, some coal and charred wood from the same source, textile fibres, with vegetable hairs and tissues of horticultural origin. The Kew deposits are more definitely horticultural and domestic, with small spheres, few in number, due to industry. A'l contain quartz sand. Leaves from a marsh around a power station burning pulverised fuel showed lodgements of spheres along the midrib, some of magnetic oxide, whilst leaves from Teddington Railway Station were covered with ferric oxide with some spheres; the ferric oxide I attribute to the erosion and corrosion of the live rails of the electrified system; few steam trains pass through this station. Dust collected from leaves and from a raised wooden platform in my garden at Teddington, contained much sand, and some coal and coke, with very few spheres. Dust from leaves in Battersea Park, near the Power Station, was mostly domestic and horticultural in origin, very few spheres being found, showing the efficiency of the gas washing plant. Ivy leaves from sheltered places around the village of Cockington, near Torquay, yielded a fine, reddish sand, with calcium carbonate, chlorides and traces of sulphates, vegetable hairs and tissues, unicellular green algæ and mycelia, but no obvious ash, coke, coal or soot.

The chemical and microscopical analyses (Table II.) of grit (a) from the roof of a London railway terminus, taken during a cleaning; (b) from the

TABLE II.

	(a)	(b)	(c)
Water			4.81
Tar (soluble in CS ₂)	1.07	2.20	
Oxidised oils (? soluble in acetone)	0.81	29.40	} 32.79
Other carbonaceous matters	28.45		
Ferric oxide	12.31	11.05	4.75
Alumina	12.25		4.40
Calcium oxide		9.11	8.65
Alkalis, etc.	3.68		
Soluble silica	1.78	14.84	} 17.97
Insoluble silicious matter	39.65	33.40	
	100.00	100.00	
Including SO ₂		9.01	9.11

inner part of the Fleche at County Hall, London; and (c) from the air washing plant of the Council Chamber, will show the nature of the disperse phases which reach a considerable height in the air of London.

Microscopical Examination.

- (a) Coal, coke, sand, spheres (glassy and bubbly, some yellow, mostly white or transparent) ferromagnetic particles.
- (b) Wood, vegetable branched hairs and other tissues, sand (rounded and sharp, ferric oxide (magnetic) with very little Fe_2O_3 , very few spheres and very little coal or coke.
- (c) Mostly amorphous coal ash, very few spheres, coke, trace of coal, felted textile fibres, plant hairs and tissues, charred wood.

The composition of dust in the underground railways of Paris is given in a report by Armand Gautier, Laveran, Vallin and Bès de Berc to *le Conseil d'Hygiène publique et de Salubrité du Département de la Seine*.¹⁹ It is interesting to note, as in the London dust from the station roof that the tunnels of the "Metro." contained large proportions of iron, whilst in the Nord-Sud organic matter predominated. See Table III.

TABLE III.

"Metro."		
Fer metallique.	46.00	soit fer total 56.15 per cent.
Oxide de fer.	14.57	
Cuivre.	traces.	
CaO (en SO_4 Ca).	12.12	
Matiere grasiere.	1.12	
Eau et matieres organiques.	12.60	par difference.
"Nord-Sud."		
Cuivre.	neant.	
Fer metallique.	traces.	
Fer oxyde.	8.06	
Soit en fer total.	5.64	
Silice, etc.	19.80	
Sulfate de chaux, CaCl_2 , etc. (en SO_4 Ca)	26.80	
Eau et matieres organiques.	45.30	

The calcium chloride is ascribed to the salt used for washing the platforms, and the organic matter to the material of the brakes.

Lessing²⁰ has given much information on the dust emitted from industrial chimneys in a paper read before the World Power Conference in 19 , and the emission of soot, ash, grit and gritty particles and the measures taken to obviate such emission is the subject of a report, published in 1932, of a Committee appointed by the Electricity Commissioners.²¹

¹⁹ A. Gautier, *Comp. Rend. Cons. d'Hyg. Pub. et du Salub. du Dept. de la Seine*, 1914, 20, 197-242.

²⁰ R. Lessing, *Fuel in Science and Practice*, Aug., 1930, 9, 348.

²¹ *Elec. Comn. Report on . . . Soot, Ash, Grit and Gritty Particles. . .* H.M.S.O., 1932.

Summary.

The dispersoids found in the air are partly normal to it. These have water for their main constituent. Others which are natural in origin, but are associated with air which has travelled over land, are living cells. The air of towns, or which has travelled over towns, contains droplets formed from the gaseous products of combustion, and tar, soot and ash from the combustion of fuel. Fine silicious matter may be found in the air of town or country. The concentrations of these dispersoids, even in highly polluted air, are very low.

GENERAL DISCUSSION.*

Mr. C. F. Goodeve (*London*): asked what was meant by the "unstable size" referred to. The discussion of the equilibrium conditions obtaining in droplets, given both by Köhler and by Dooley and the speaker in papers to this discussion, indicates the existence of no such unstable size with the properties described by Dobson.

Professor F. G. Donnan (*London*) said he thought that modern workers would do well to study the classical work of Willard Gibbs on the thermodynamics of "surfaces of discontinuity." It was extraordinary how little people knew about the profound investigations of Gibbs on the formation and stability of films and liquid drops.

Professor H. Köhler (*Uppsala*), in introducing his paper, added:

(1) The latent heat of condensation, λ , mentioned on page 1157, is derived as follows:—

The energy equation requires

$$q = dU + A p dv \quad . \quad . \quad . \quad (1)$$

where U is the internal energy of the system and $A p dv$ the work in heat-units performed by the system. We now bring in T and x as independent variables:

$$dU = \frac{\partial U}{\partial x} dx + \frac{\partial U}{\partial T} dT \quad \text{and} \quad dv = \frac{\partial v}{\partial x} dx + \frac{\partial v}{\partial T} dT.$$

Dividing (1) by T , we obtain the change of entropy dE .

$$dE = \frac{q}{T} = \left(\frac{\partial U}{\partial T} + A p \frac{\partial v}{\partial T} \right) \frac{dT}{T} + \left(\frac{\partial U}{\partial x} + A p \frac{\partial v}{\partial x} \right) \frac{dx}{T}. \quad (2)$$

Since dE is a whole differential, we get:—

$$q = C dT + AT \left(\frac{\partial p}{\partial T} \cdot \frac{\partial v}{\partial x} - \frac{\partial p}{\partial x} \frac{\partial v}{\partial T} \right) dx. \quad (3)$$

In (3) the latent heat of condensation is:—

$$\lambda = AT \left(\frac{\partial p}{\partial T} \cdot \frac{\partial v}{\partial x} - \frac{\partial p}{\partial x} \frac{\partial v}{\partial T} \right).$$

If, now, we insert the tension and the specific volume of the drops and the vapour, we get:—

$$\lambda = \lambda_0 + \frac{2ATw'}{r} \frac{\partial}{\partial T} \left(\frac{s}{T} \right) - AR_1 T \times \frac{\partial \log e}{\partial x}.$$

The latent heat of condensation on droplets of a solution, λ , is derived without assuming any change of the entropy, but from the energy equation and from the fact that dE is a whole differential.

(2) The number, N , of droplets mentioned in my paper is the same as the number of nuclei accompanying the rising air, and the system is cooled

* On the three preceding papers.

adiabatically. On this assumption, the process is reversible. One must remember that change of entropy is entirely determined by the initial and terminal values. I have not examined isothermal processes.

(3) According to theory, a relation should exist between the concentration and the number N . This I have never found experimentally. I therefore conclude that the growth of droplets must take place otherwise; if coalescence take place (or evaporation from some droplets and simultaneous condensation on others) the process is irreversible.

Mr. C. F. Goodeve (*London*): Asked why Köhler applied thermodynamical equilibrium considerations to his droplets but denied that equilibrium obtained during the condensation of the fog to form hoar frost. *Microscopic* investigations could not *prove* that the hoar frost had the same composition as the fog from which it was deposited, and experiments in other cases have shown that equilibrium conditions are very rapidly set up. The speaker considered it essential to prove this point before consideration could be given to the extensive data obtained by Köhler.

The whole-number rules were very interesting, and further experiments showed intermediate series. How was it possible to reconcile this whole-number rule with the thermodynamical considerations given later in the paper?

The conclusion with regard to the latent heat of evaporation in the unstable region (where the slope was negative), Fig. 1, is of doubtful validity. Droplets in this region are very unstable, as is pointed out in a later paper by Dooley and Goodeve. It is not useful to apply entropy considerations to a system which is essentially irreversible.

Mr. J. H. Coste (*Teddington*) said: The chlorion content of rainwater has been determined in many places. I think Professor Köhler would find much information in Clarke's *Data of Geochemistry*. The water of large rivers in tropical districts, and of upland streams, is of the order given by Professor Köhler for rainwater, which would be expected. I find, on looking at the analyses published by the Atmospheric Pollution Research Committee that there is a tendency for the chlorion content of rainwater in towns to be higher in winter than in summer. How far this is due to salt brought in by wind from the sea, or alternatively to chlorine from coal is difficult to say, but the halide content of fuel is by no means negligible.

Professor F. G. Donnan (*London*) said that some eminent landscape painters had drawn his attention to the haze which always existed in England with an East wind. He could confirm these observations from his own experience. His artist friends found it impossible to paint when the East wind (fine weather) haze blotted out all detail. As soon as the wind changed to the South or West, this particular haze disappeared. Was it due to Continental or other dust nuclei which remained in suspension in the relatively dry air-currents of the East wind, and which were rapidly deposited by adsorption or absorption of water from the moist, southerly and westerly air-currents?

This peculiar and very intense haze was quite different from ordinary mists or fogs, or from the well-known "sea frets" which sometimes invaded the land areas.

Dr. F. T. Peirce (*Manchester*) said: Would the landscape painter distinguish between light scattering by particles and refraction by convection currents, which may be more pronounced in East wind weather when the upper air is cold and the ground warmed by bright sunshine?

Dr. R. Meldau (*Berlin*) said: Almost a hundred years ago, Chr. G. Ehrenberg described "the abundant invisible air-borne organic life" which he had studied, described and pictured over a period of many decades.¹ Svante Arrhenius developed along similar lines the hypothesis of the

¹ *Abhand. Königl. Akad. Wiss., Berlin, 1871 et seq.*

Panspermie (*Allbesamung*). It might perhaps be useful to review the old work of Ehrenberg in the light of modern knowledge.

Dr. W. H. J. Vernon (*Teddington*) (*communicated*): An indication of the nature of dispersoids in country and town air is afforded by the wind-borne constituents of certain metallic corrosion products, *e.g.* the familiar green patina on copper.²

ANALYSIS OF WIND-BORNE MATERIALS IN THE GREEN PATINA ON COPPER FROM TYPICAL SOURCES.

	N. Mims Spire, Hert- fordshire.	Bodleian Library Roof, Oxford.	British Museum Dome, London.	Customs House Dome, Ramsgate.
Per cent. wind-borne matter in green patina	9.6	6.9	19.2	4.3
<i>Per Cent. Constituents in Wind-borne Matter.</i>				
Iron oxides (as Fe_2O_3)	43.0	64.3	24.2	36.6
Alumina, Al_2O_3	47.4	13.4	37.0	17.0
Carbonaceous matter	6.4	11.9	32.6	9.7
Siliceous matter	3.2	10.4	6.2	36.6

The high proportion of iron oxide and alumina is striking, although it is difficult to deduce any topographical relationship: well-marked maxima are exhibited by carbonaceous matter in the town sample, and by siliceous matter in the marine sample.

The nature of the dispersoids has also a great influence in determining the composition of the main part of the product, *i.e.* the part derived from corrosion of the underlying metal. The characteristic constituent in country atmospheres (in Great Britain) is basic copper sulphate, derived mainly, no doubt, from the action of sulphur dioxide either in gaseous or dispersoid form, although ammonium sulphate particles must play a subsidiary part.³ In town atmospheres the proportion of basic copper carbonate is very greatly increased, rising to nearly 25 per cent., compared with 2.7 per cent. in rural atmospheres, due in part at least, to a higher proportion of carboxylic acids in town air,⁴ almost certainly in dispersoid form; but, as suggested by Mr. Coste,⁵ this factor is probably supplemented by the greater amount of calcium carbonate diffused into town air, from mortar, cement, limestone, etc.

Although particles of chlorides derived from the sea provide effective nuclei for rain drops at much greater distances, they cease to be effective from the corrosion point of view at comparatively short distances from the sea, unless they are favoured by prevailing winds. Thus, at inland sites in this country chlorides are absent from the copper patina. In samples taken in mid-Wales, 30 miles from the sea, there is 20.75 per cent., and at Dundalk, on the north-east coast of Ireland, only 8.1 per cent. basic copper chloride. The occurrence of the greater chloride at the greater distance from the sea is here clearly attributable to the influence of prevailing winds.

It seems right to emphasise the undoubted importance of dispersoids in atmospheric corrosion phenomena, especially as this aspect has not been formally represented elsewhere in the discussion. The fundamental part

² Vernon and Whitby, *J. Inst. Metals*, 1930, 44, 389.

³ G. F. New, J. S. Owens, W. H. J. Vernon, *ibid.*, 1932, 48, 130, 137, 140.

⁴ W. H. J. Vernon, *J. Chem. Soc.*, 1934, 1853.

⁵ J. H. Coste, *J. Soc. Chem. Ind. (Chem. and Ind.)*, 1934, 53, 1061.

played in the corrosion of iron by suspended particles (sufficiently small to have Brownian movement and capable of interception by a simple muslin screen) was demonstrated by the writer some years ago,⁶ and its importance has been amply confirmed in more recent experiments.⁷

Professor H. Köhler (*Uppsala*), in reply, said: Without doubt there are different kinds of hygroscopic nuclei in the atmosphere. According to my calculations, the larger nuclei of a definite kind must first be considered, and then smaller and smaller: the mass is decisive. If different kinds of nuclei are present, however, the mass is not of paramount importance, but their respective hygroscopic powers also come into consideration. In large towns and industrial countries the atmosphere gains many very hygroscopic nuclei, are emitted into the atmosphere, and these have the same effect as the less hygroscopic seasalt.

My results on condensation and the constitution of clouds, appear to conflict with thermodynamics, which has not been uncommon in meteorology since Hertz 1884. If we assume that condensation on adiabatic expansion of the air takes place on nuclei which are present, results are obtained which do not correspond with reality. Droplets cannot grow by continuous condensation to the size of raindrops, or even to that of cloud droplets.

The latent heat of condensation is deduced for condensation on droplets consisting of pure water.⁸

The vapour tension of the droplets of solutions for the condition $\alpha^2 < \alpha_1^2 \cdot 2^{-12}$ decreases or to some extent is almost constant on adiabatic cooling, it is also a function of T . Smaller seasalt-nuclei than $\alpha_1^2 \cdot 2^{-12}$ are not available for the condensation in the atmosphere, because too great supersaturation then would be necessary. It is also important when considering equilibrium conditions to define accurately the vapour tension of a droplet present in the atmosphere, with regard to the measured mean value of the pressure of the water vapour.

The constitution of the hoar-frost deposited from fog, has been examined in other than microscopic ways and the same results were always obtained.⁹

Mr. J. H. Coste (*Teddington*), in reply, said: Sir Robert Robertson had informed him in correspondence of the work on products of combustion to which he referred at the meeting. It was interesting to receive this confirmation of the frequent presence of nitrous acid in air contaminated with smoke from chimneys. Dr. Vernon's figures seemed to show that wind-borne matters, and especially silicates and carbon were more prevalent in town air.

As to the products of corrosion of copper he was inclined to think that the basic copper sulphate was a residual product, since he had found crystals of normal copper sulphate, on copper surfaces exposed to the air and dew, but not to the leaching effect of rain.

He was very interested in what Dr. Meldau had to say about Ehrenberg, whose microscopical work was well known, with whose researches on atmospheric dispersoids he was not acquainted. The early microscopist, Leowenhoeck, had made some evidently very careful examination of the dispersoids in rainwater, and Angus Smith had done a great deal. He would seek the opportunity of reading Ehrenberg's papers.

⁶ W. H. J. Vernon, *Trans. Faraday Soc.*, 1927, **23**, 159.

⁷ *Ibid.*, 1935, **31**, 1678.

⁸ W. Voigt, *Thermodynamik*, II Band, p. 134.

⁹ See my papers from 1921 to 1933 and also the examination of rain made by Israel and Niederdorfer.

THE DETERMINATION OF THE MASS AND SIZE OF ATMOSPHERIC CONDENSATION NUCLEI.

BY J. J. NOLAN AND V. H. GUERRINI.

Received 6th February, 1936.

In 1903 J. J. Thomson¹ and Langevin² independently demonstrated the possibility of the existence in a non-saturated atmosphere of stable drops of water of diameter of the order 10^{-6} cm. In 1905 the large atmospheric ions were discovered by Langevin and were found to be of a certain degree of homogeneity as regards their mobility. It was natural, then, to assume that the large ions were the condensation nuclei, familiar owing to the work of Aitken, which had acquired positive and negative charges, and that the condensation nuclei were the stable uniformly-sized drops, the theoretical possibility of which had been indicated. Whatever be the nature of the condensation nuclei, the identification of the large ions with the charged nuclei may be said to have been firmly established by all later work.

In 1917, J. J. Nolan showed³ that, assuming the large ions to be spheres of water, calculations of their size made by a kinetic-theory formula due to J. J. Thomson and by Millikan's modification of the Stokes-Cunningham formula were in good agreement. For ions of mobility 0.00033 cm./sec. in a field of 1 volt/cm., assumed to carry unit electronic charge, the radius calculated was 4.1×10^{-6} cm. The fact that the charge on the large atmospheric ion is normally the electronic charge was afterwards demonstrated.⁴ More recently, J. J. Thomson and G. P. Thomson,⁵ from calculations somewhat similar to those already referred to, obtained the value 4.5×10^{-6} cm. An interesting calculation of a different kind might be mentioned. By attributing the absorption of solar radiation to the condensation nuclei, P. J. MacLaughlin⁶ from experiments made at the top and bottom of the Eiffel Tower, calculated a value 5.5×10^{-6} cm. for the radius of the nuclei.

The possibility of making more precise measurements of the nuclei was disclosed as a result of some observations⁷ directed in the first instance towards the investigation of the manner in which nuclei are lost from an air-stream flowing through tubing. It appeared that the loss of nuclei could in general be attributed to two effects, gravity and diffusion to the walls. It was possible also in general to separate these effects, to estimate the amount of each separately, and hence to deduce the terminal velocity of fall of the nuclei and their diffusion coefficient in air.

¹ J. J. Thomson, *Conduction of Electricity in Gases*, 1st ed., 1903, p. 149.

² P. Langevin, *Cours de Collège de France*, 1903-04, vide A. B. Chauveau, *Le Radium*, 1912, 9, 161.

³ J. J. Nolan, *Proc. Roy. Soc.*, 1917, 97A, 112.

⁴ J. J. Nolan, R. K. Boylan and G. P. de Sachy, *Proc. Roy. Irish Acad.*, 1925, 37, 1.

⁵ J. J. Thomson and G. P. Thomson, *Conduction of Electricity in Gases*, 3rd ed., 1928, p. 189.

⁶ P. J. MacLaughlin, *Comptes rendus*, 1927, 184, 1183.

⁷ J. J. Nolan and V. H. Guerrini, *Proc. Roy. Irish Acad.*, 1935, 43, 5.

Experimental Methods.

In order that the losses of nuclei should be sufficient to enable accurate observations to be made, it is necessary that the air carrying the nuclei should pass very slowly through a rather narrow channel. The most convenient way to secure this is to cause the air to flow in a thin sheet between parallel plates. By building up a pile of plates with suitable separators, several such air-sheets may be arranged to flow in parallel. When the planes of the plates are horizontal, the loss of nuclei is due both to diffusion and fall. When the plates are set with their planes vertical, the loss by fall is negligible and diffusion alone may be held to operate.

In our experiments a water-sealed gasometer of capacity about 500 litres was filled with a mixture of filtered air and atmospheric air containing the nuclei under examination. The air in the gasometer, having a concentration of about 5000 nuclei per cm^3 was driven, under a suitable head of pressure through the parallel-plate system. At the inlet and outlet of the system, the number of nuclei per cm^3 of air was counted by an Aitken apparatus. Each determination of velocity of fall and of diffusion coefficient involved a large number of readings of the Aitken instrument at each end of the apparatus under the two conditions of plates horizontal and plates vertical.

Calculation of V_g , the Velocity of Fall.

If we assume a uniform concentration of nuclei in the air entering the apparatus and conditions of stream-line flow in the space between the

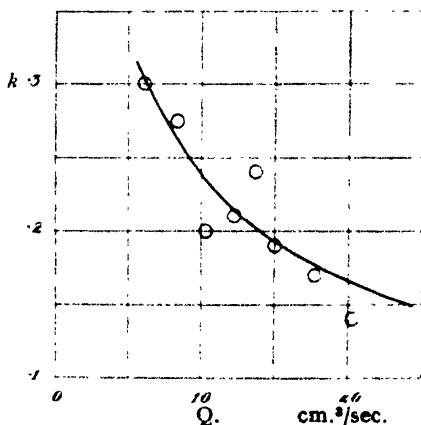


FIG. 1.

plates, it is easily shown that the fraction k of nuclei lost is connected with the terminal velocity V_g by the relation

$$V_g = \frac{6Q}{Lb} \left(\frac{k^2}{2} - \frac{k^3}{3} \right),$$

where Q is the volume of air passing per second between the plates, L is the horizontal length and b the breadth of the space.

Since the quantity k (fraction of nuclei lost by fall) is obtained as the difference between the fractions lost in the horizontal and vertical positions of the plates, it is in general small, and is not readily determined to a high degree

of accuracy. The amount of agreement between the experimental and the theoretical loss by fall obtainable under favourable conditions may be judged from Fig. 1, in which values of k obtained with various values of the air-stream are plotted. The continuous curve shows the theoretical relation between the quantities for an assumed velocity of fall of 8×10^{-5} cm./sec.

Calculation of D , the Coefficient of Diffusion.

It has been shown⁷ that the loss of particles by diffusion from air flowing through a thin rectangular channel may be expressed in the form

$$\frac{n}{n_0} = 1.066 \exp. \frac{-3.67bDz}{aQ} + 0.0065 \exp. \frac{-44.4bDz}{aQ},$$

where n/n_0 is the ratio of the concentrations of the particles in the air entering and leaving, b is the breadth, z the length and a the half-depth of the channel and Q is the volume of air passing through per second. Since the second term will, in practice, always be negligibly small, the relation can be expressed as

$$n/n_0 = 1.066 \exp. -x, \text{ where } x = 3.67 bDz/aQ.$$

From the nature of the observations, it is to be expected that the determinations of D , the diffusion coefficient will be of a higher order of accuracy than those of V_0 . The values found do, in fact, exhibit a higher degree of consistency. Fig. 2 shows values of n/n_0 , obtained

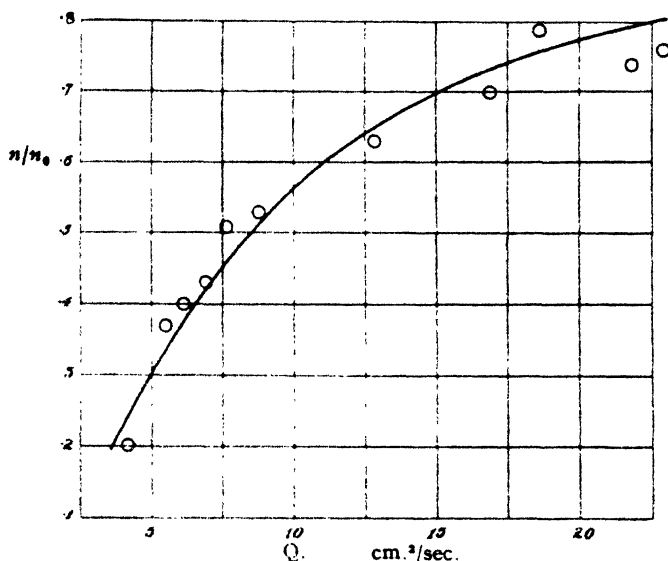


FIG. 2.

under conditions not specially favourable, plotted against Q , the volume of air passing per second. The continuous line shows the theoretical relation between the quantities for an assumed value $D = 18 \times 10^{-8}$ cm.²/sec.

It appears generally from our observations that the loss of nuclei can be completely accounted for by the two processes of fall and diffusion, and that the processes can be separately observed. In our experiments three sets of apparatus differing widely in dimensions were used. The particulars of the materials and dimensions of these are set out in the following table:—

Appa- ratus.	Material of Plates.	Thickness of Plates.	Length.	Breadth.	Depth.	Number of Channels.
I	Glass	0.211 cm.	76 cm.	19.0 cm.	0.211 cm.	7
II	Duralumin	0.046 "	100 "	24.9 "	0.642 "	7
III	Brass	0.054 "	30 "	9.9 "	0.054 "	10

The results of observations made on nuclei in Dublin air are collected in the following table. It should be stated that the air was not drawn

directly from the open. It was room air, not contaminated in any way, but differing from atmospheric air in that the nuclei in it were older on the average than those in the outside air.

Apparatus.	$V_g \times 10^6$, cm./sec.	$D \times 10^6$, cm. ² /sec.	The values set out in this table are means derived from figures which, especially in the case of V_g , show very considerable scatter. This variation in the values found may be regarded as due in part to the inherent experimental difficulties, and in part to the fact that the observations were spread over many months, with very varied weather conditions, and possibly considerable real variation in the character of the nuclei. It is satisfactory that the mean values found with the different apparatus are in fair agreement. We may conclude with a certain measure of assurance that the values V_g and D for the nuclei we have been observing are close to
I. 1st Series	8.6	17.5	
2nd "	6.9	18.1	
II.	8.2	20.9	
III.	7.2	17.4	

the inherent experimental difficulties, and in part to the fact that the observations were spread over many months, with very varied weather conditions, and possibly considerable real variation in the character of the nuclei. It is satisfactory that the mean values found with the different apparatus are in fair agreement. We may conclude with a certain measure of assurance that the values V_g and D for the nuclei we have been observing are close to

$$\text{and } V_g = 7.5 \times 10^{-5} \text{ cm./sec.} \\ D = 18 \times 10^{-6} \text{ cm.}^2/\text{sec.}$$

Calculation of Mass and Size.

The well-known Einstein equation gives the mobility, *i.e.* the ratio of the velocity of a particle through a gas to the force acting on it $= DN/RT$ we have therefore

$$\frac{V_g}{mg} = \frac{DN}{RT} \quad \text{and} \quad m = \frac{V_g}{D} \cdot \frac{RT}{ng}.$$

The mass of the nuclei observed in our experiments is therefore

$$m = \frac{7.5 \times 10^{-5}}{18 \times 10^{-6}} \cdot \frac{831 \times 10^5 \times 288}{6.06 \times 10^{23} \times 980} \\ = 1.68 \times 10^{-16} \text{ g.}$$

If we assume that the nuclei are spherical we can write the Einstein equation in the form

$$D = \frac{RT}{N} \cdot \frac{1 + l/a (A + B \exp. - ca/l)}{6\pi\eta a}.$$

Knowing the constants in this equation, we can use it to calculate a for different values of D . Values of A , B and c have been given by Millikan⁸ and Mattauch.⁹ While these values differ, they give, over the range with which we are concerned, curves of D against a which are practically identical. From these curves we find for $D = 18 \times 10^{-6}$, $a = 2.85 \times 10^{-6}$ cm. The volume of such a particle will be 0.97×10^{-16} cm.³. Comparing this with the value 1.68×10^{-16} gr. found for the mass, we arrive at $1.68/0.97 = 1.7$ for the density of the nuclei.

Effect of Time.

The values for mass and radius which we have just given are calculated from the results of a great many experiments, all made on room air, and refer therefore to nuclei to some extent aged. During the

⁸ R. A. Millikan, *Physic. Rev.*, 1923, **22**, 1.

⁹ J. Mattauch, *Z. Physik.*, 1925, **32**, 439.

duration (about two hours) of each experiment, the nuclei were contained in a water-sealed gasometer. There was no indication that, during the time of the experiment, any change in the nuclei occurred. On long standing however the evidences for change are quite definite. There is a reduction in the values of both V_0 and D . If V_0 and D fell off at the same rate, *i.e.* so as to keep V_0/D constant, it would mean that the nuclei were increasing in size, but that their mass was remaining constant. Our observations made so far tend to show that V_0 diminishes more rapidly than D , so that it would appear that the nuclei surviving after a certain lapse of time are (1) larger, (2) of smaller mass, and therefore (3) of considerably lower density than the average at the beginning. It may be noted that P. J. Nolan¹⁰ found that nuclei stored in the same way showed an increase with time in their coefficient of combination with small ions. These results are consistent with the supposition that the nuclei present originally are a mixture of different kinds, and that those observed after a lapse of time are the larger and lighter ones which have escaped loss by diffusion and fall.

Observations on Nuclei in Country Air.

We have made a number of observations on nuclei in the air at Glencree in the Wicklow Mountains, eleven miles south of Dublin. Here the concentration of nuclei varies over a wide range, large numbers being found when the air-supply comes from the direction of Dublin, while small numbers are usually found when the wind comes from the open country to the south and west. The results found so far indicate the possibility of a considerable range of variation in the sizes and masses of the nuclei. Observations are being continued with the object of determining the effect of the size of the nuclei on the control which they influence on the equilibrium of atmospheric small ions.

¹⁰ P. J. Nolan, *Proc. Roy. Irish Acad.*, 1929, 38, 49.

GENERAL DISCUSSION.

Professor F. G. Donnan (*London*) said he thought that the work of Professor Nolan and Dr. Guerrini represented a very important contribution to the problem of the nature of atmospheric condensation nuclei.

Dr. G. M. B. Dobson (*Oxford*) said: The minute particles seen in the normal atmosphere by the aid of the ultra-microscope appear to be of various sizes. Indeed, it would be very surprising if they were all closely the same size, as assumed by Professor Nolan in his calculations. In his observations with the plates of the instrument horizontal the particles which settle out will be chiefly the larger ones, while with the plates vertical the smaller particles will diffuse to the sides most rapidly. Thus, if the particles present have a large range of size his equations will not hold strictly.

I should like to suggest to Professor Nolan that he should make calculations to see what would be the effect on the results obtained if there were really present particles of many sizes. Thus, it would be interesting to know how the size he would obtain by the present method would differ from the true average size of the particles present.

Professor R. Whytlaw-Gray (*Leeds*) said: The distinction usually made between atmospheric nuclei and finely dispersed solid matter appears to me to be an artificial one. It is supposed that the former, on account of their hygroscopic character, condense moisture readily and form minute droplets, whilst the latter do not behave in this way at all, or do so only

with difficulty. For this reason the Aitken counter is supposed to innumerate the hygroscopic nuclei only, and the Owens' dust counter and the thermal precipitator the larger particles of solid material which are of microscopic dimensions.

Experiments made here with the Aitken instrument indicate that solid particles of such materials as silica, magnesium oxide, finely divided carbon, etc., readily act as condensation nuclei and can be counted and it seems probable that this method reveals not the hygroscopic nuclei only but the total number of particles of all kinds that are present.

Again, the view is often expressed that nuclei are of amicroscopic dimensions and hence are invisible in the ultramicroscope. Some of them no doubt fall into this category, but many nuclei and large ions can be seen and counted with the latter instrument. Support for these views is afforded by a comparison recently made in this laboratory of the Aitken counter with the ultramicroscope on a number of smokes and dusts. With smokes of stearic acid, carbon black, and paraffin, as well as with silica dusts, a close agreement was found. With ordinary Leeds air containing the usual amount of suspended pollution, the Aitken instrument counted about 30 per cent. more particles but when the air was enclosed in a large tank and comparisons made at intervals over a long period, the numbers counted became closer with lapse of time and at the end of three hours were approximately equal by the two methods.

These experiments appear to show that particles of various kinds and of a considerable size range are present in town air. Of these a certain proportion are amicroscopic and a much smaller proportion of microscopic dimensions. The most numerous are those which are usually classed as ultramicroscopic and fall approximately between the size limits of 5×10^4 and 2×10^{-8} cms. radius, i.e., between 0.05 and 0.2 μ .

The total number of particles observed in Leeds air when these experiments were made, was of the order of 10^5 per c.c. Those visible microscopically in the thermal precipitator records numbered about 3000 per c.c.

Professor F. A. Paneth (*London*) said: On the question whether particles of different size are to be found in air, I should like to know the opinion of meteorologists concerning the presence of particles too small to be seen even under the ultra-microscope. So far as I am aware, such particles have been postulated only by chemists, as a means of explaining variations in the density of air found in 1893 by Lord Rayleigh and more recently (1917) confirmed by Ph. A. Guye in Geneva; according to Guye, the weight of 1 litre of air can vary by several tenths of a milligram. If due to a difference in composition, this would correspond to a change in the oxygen percentage of more than 0.1 per cent. by volume which, of course, could readily be detected chemically; it is impossible to ascribe the density variations to any other alteration of the chemical composition of air. They seem to be connected with changes in the barometric pressure, and Guye suggests that the assumption of extremely fine particles of dust may provide an explanation. This, of course, is an *ad hoc* hypothesis made only after the failure of all other attempted explanations, and I wonder whether any meteorological observation can be quoted in its support.

Professor R. Whytlaw-Gray (*Leeds*) said, in reply: It is difficult to imagine any kind of fine particulate system present in air which would alter the density by as much as a few tenths of a milligram per litre, i.e., by a few parts in 10,000; the variation reported by Guye in the experiments quoted. In a fine smoke containing about 10^4 particles per c.c. an average value for the mass concentration is of the order of 20 milligrams per cubic metre. This could only alter the density by 1 part in 70,000, though its presence would be evident in the Tyndall beam. If the air were optically empty the particles would have to be about ten times smaller and even this small variation in weight would require a number concentration of 10^8 per c.c. which seems very unlikely.

Mr. G. W. Slack (*Leeds*) said: A variation of only one-tenth of a milligram corresponds to a mass concentration of one hundred milligrams per cubic metre and whilst a cloud of this concentration could no doubt be prepared which would give no sign of its presence in the Tyndall beam or ultramicroscope there can be little doubt that it would aggregate sufficiently to do this in a very short time, and so it is unlikely that this is the explanation of the observed variations.

Mr. A. G. Grant (*Darlington*) said: Has any attempt been made to define the properties of a nucleus? Previous papers have referred to hygroscopic nuclei, for example, sea-salt, and it has often been suggested that organic spores and particles of free carbon (in industrial fogs) may form nuclei. Professor Nolan's paper deals with molecular aggregates which are presumably somewhat bigger than Langevin ions. Are these aggregates credited with condensation properties resembling the hygroscopicity of sea-salt, or is there some more basic attribute which determines whether or not the smallest aggregates of matter may serve as nuclei?

Mr. J. H. Coste (*Teddington*) said: There seems no reason, in the nature of things, why hygroscopic nuclei should, in the air of inhabited districts, be all of the same kind or size. Wright and I have found various ions (in the chemical sense) in the condensates from London air, with some evidence of selective condensation. Professor Nolan has said that the density of 1.7 of the nuclei is not a figure on which much reliance can be placed, although it is of the right order. It would correspond to very strong solutions of any likely salt or hydride, and seems to be too high.

Mr. C. H. Bosanquet (*Billingham*) said: Are the diffusion and fall effects additive? It appears probable that the increase of particles striking the lower plate would be almost compensated by the decrease on the upper plate, if the velocity of fall is small. If this is the case, erroneous values of V_f would be obtained by applying the formula for k given in the paper directly to the values of k obtained by difference.

Dr. J. J. Nolan (*Dublin*), in reply, said: We have not been concerned in this work very directly with the nature of the condensation nuclei, but rather with an essay at the determination of the sizes of the bodies—whatever they may be—which are counted by the Aitken instrument. We have hitherto accepted the sharp distinction, apparently established by the work of Wigand and Boylan, between the condensation nuclei and the true dust. The question, however, is obviously an open one, and we await Professor Whytlaw-Gray's further results with great interest.

In the course of correspondence, it has been pointed out to us by Mr. Bosanquet that in the calculation⁷ of V_f , while we have allowed for the difference in air-velocity in different levels of the air-stream, we have not taken account of the same difference as affecting the velocity of entry of particles into the apparatus. This consideration gives a simpler expression for V_f , and as a result of the correction (while a greater degree of coherence appears among the values calculated for different air-velocities), the results for velocities of fall are approximately doubled.

From experiments now in progress on atmospheric air contained in oil-sealed gas-holders, we hope to obtain a truer idea of the distribution of sizes of nuclei in the free atmosphere.

HYGROSCOPIC NUCLEI IN THE FORMATION OF FOG.

BY JAMES C. PHILIP.

Received 9th March, 1936.

The fogs which have been the subject of investigation by the author and his collaborators¹ are those obtained on passing an air stream charged with a volatile acid through a solution of alkali hydroxide containing a trace of volatile alkali. When, for example, filtered air is drawn through concentrated hydrochloric acid and then through a solution of sodium hydroxide to which a trace of ammonium chloride has been added, a fog is produced in the alkali vessel, and this fog, once formed, is extraordinarily persistent. It can be passed through water without more than partial absorption and although passage through strong sulphuric acid appears to clear up the air stream, the fog reappears on subsequent bubbling through water.

The fog droplets can be removed from the air stream by woolly asbestos and submitted to analytical examination. This shows them to contain ammonium chloride and free hydrochloric acid and the weight of fog, obtained in a standard run, has been found to vary in a significant manner with the concentration of the alkali solution and with the amount of ammonia which it contains. The formation of fog can be detected even when the proportion of ammonia in the alkali solution is as low as 1 part in 10 million. Indeed, the production or non-production of fog under the conditions stated, provides as delicate a test for the presence of ammonia as the well-known Nessler reagent.

Our view of this phenomenon is that as the bubble of the air-HCl stream forms on the end of the inlet tube in the alkali solution molecules of ammonia from the latter combine with molecules of hydrogen chloride in the bubble producing nuclei of ammonium chloride; water then condenses on these hygroscopic nuclei, and the droplets so formed absorb free hydrogen chloride. On the bubble rising to the surface the suspended droplets escape into the vapour space above the solution, thus giving rise to the fog.

The point with which this communication is more particularly concerned is the question of the mechanism of formation of the droplets. Light is thrown on this matter by studying the manner in which the weight of fog and its composition are affected, under otherwise steady conditions, by changes in the vapour pressure of the alkali solution. As this vapour pressure is reduced it will be increasingly difficult for the nuclei to acquire water, and the weight of the fog droplets obtained in a standard run will decrease. Such a result has been obtained with sodium hydroxide solutions of greater strength than 1·0*N* concentration, but the most interesting evidence was provided by a series of experiments in which the vapour pressure of the alkali solution was reduced by the addition of sodium chloride.

¹ Askew, *J. Chem. Soc.*, 1927, 966; Aldis and Philip, *ibid.*, 1930, 1103; Jackson and Philip, *ibid.*, 1934, 341.

The data recorded in Table I. were obtained in a series of experiments¹ all carried out with $N/1$ NaOH solution containing 0.001 per cent. NH_3 , but differing in the content of sodium chloride. It should be noted that each figure in the second column includes 80-90 mg., due to the water vapour.

TABLE I.

NaCl, g.-equiv./l.	Weight of Fog + Water Vapour mg.	Found in Fog.	
		HCl (free), mg.	NH_3 (as NH_4Cl), mg.
0	467	35.9	0.64
1.0	457	37.0	0.64
2.0	389	33.4	0.65
3.0	310	28.4	0.65
4.0	217	18.9	0.66
5.0	140	12.0	0.66

The figures in the foregoing Table clearly indicate that as the fog obtained in a standard run gets thinner the amount of acid which it contains falls off steadily, whereas there is no sign of decrease—there is in fact a slight increase—in the amount of

ammonia carried over as ammonium chloride. It seems reasonable to conclude that the hydrogen chloride carried over depends on the water content of the fog droplets and that if the water-vapour pressure of the liquid in the fog-chamber could be reduced much further, nuclei of ammonium chloride would still be produced which, however, would be both dry and neutral.

Observations confirmatory of those in Table I. were obtained with triethylamine as the volatile alkali instead of ammonia.² In the series detailed in Table II. the air-HCl stream was passed in each case through a solution which was 0.5N as regards sodium hydroxide and contained 0.0009 per cent. triethylamine. The solutions, however, were progressively richer in sodium chloride.

Here again, as the water-vapour pressure of the solution in the fog-chamber decreases the free acid carried over in the standard run falls steadily, whereas the quantity of amine tends to rise.

TABLE II.

NaCl gm. — equiv./lit.	Wt. of Fog + Water Vapour (in mg.).	In Fog.	
		HCl Free mg.	Amine mg.
0	524	36.7	0.65
1.0	459	34.7	—
2.0	385	30.7	0.66
3.0	297	24.4	—
4.0	182	14.8	0.67

A relevant qualitative observation may also be recorded. A dried air-HCl stream was passed through a 50 per cent. NaOH solution containing 0.001 per cent. NH_3 , then through two sulphuric acid bubblers and then through water. Nothing was

visible above the sodium hydroxide solution, but fog appeared in the water vessel. It contained no detectable free acid.

The foregoing evidence certainly supports the view that the primary event in the production of the fogs is the formation of nuclei of ammonium chloride followed by the condensation of water on these nuclei, giving a solution of salt. Only then does the absorption of hydrogen chloride begin. It is true that ammonium chloride is usually regarded as non-deliquescent, but the description is not an absolute one, for the possibility of deliquescence depends not only on the nature of the salt

¹ Jackson and Philip, *loc. cit.*¹² Banfield, *unpublished experiments*.

but also on the vapour pressure of its saturated solution and on the relative humidity of the surrounding atmosphere. Further, when the salt is in an extremely finely divided state, as in the present case, and has therefore a relatively large surface exposed, the rate of adjustment of equilibrium between the salt and the water vapour in the surrounding atmosphere will be very high. The experiments of Owens⁴ on the conditions of deliquescence of minute crystals exposed to air of different relative humidity have shown that in the case of such salts as sodium chloride and ammonium chloride there is, in fact, a rapid adjustment of equilibrium.

⁴ *Proc. Roy. Soc.*, 1926, 110A, 738.

GENERAL DISCUSSION.

Mr. C. F. Goodeve (*London*) said: Professor Philip and his co-workers have been studying a very interesting type of mist and have developed a satisfactory explanation, involving the formation of a nucleus of ammonium chloride. It is to be hoped that they will now put their theories to a quantitative test. Some of the ways in which this can be done have been indicated in a paper by Dooley and myself.

It seems likely that the hydrochloric acid mist formed under the conditions of their experiments was in equilibrium with the vapour over the solutions which they used. Neglecting the effect of curvature, the vapour pressure of a solution of hydrochloric acid, as indicated by the 2nd and 3rd columns in Table I. should be the same as that of the NaCl-NaOH solution given in column 1. I have calculated the vapour pressures of these solutions (by adding the vapour pressure lowering of each compound) and in general have found that there is not good agreement between the values so calculated. It seems that there may be some disturbing factor present in their experiments.

No explanation has been given of the constancy of the ammonia content in the mists (last column, Table I.). It seems that this may be due to either or both of two causes. If the reaction between HCl and ammonium in the gaseous phase is very fast, the concentration of ammonia will be negligibly small. The amount appearing in the mist will therefore be governed by the rate of evaporation of ammonia from a solution of a certain strength into a gaseous space free from ammonia. This rate will probably be independent of the sodium chloride concentration and, therefore, a constant value is to be expected. On the other hand, the amount of ammonia in the mist is 80 per cent. of the total originally present in the liquid, and, as the rate of evaporation is probably directly proportional to the concentration of ammonia, a smoothing out of any variation would result from its deficiency.

The condensation of water and hydrogen chloride on the ammonium chloride nuclei must occur simultaneously as the vapour pressure of water on the droplet must always be below that of the solution before it is able to take up more water.

Mr. J. H. Coste (*Teddington*) said: The concentration of HCl in the fog water seems to have been fairly constant around 8 per cent., with a tendency to be greater in the fogs containing less ammonium chloride, suggesting that the droplets when formed absorbed a proportion of HCl, mainly determined by the concentration of gas, but also by the concentration of chlorides already existing in the droplets. Wright and I found that hydrochloric acid alone evaporated into nucleus-free air did not produce nuclei, which could be counted in the Aitken counter, although Helmholtz found that it did produce the "blue" cloud when mingled with steam issuing from a jet.

Professor J. C. Philip (*London*) said, in reference to Mr Goodeve's suggestion of some disturbing factor in the experiments: The results of these experiments, carried out under specified and controlled conditions, were perfectly definite and regular, and the want of agreement between the calculated vapour pressures was probably due to the uncertainty of the assumptions underlying the calculations.

He agreed with Mr. Goodeve's view that the amount of ammonia in the mist would be governed by the rate of evaporation of ammonia from the alkaline solution. It was probable, however, that the escaping tendency of the ammonia would, if anything, increase with the sodium chloride concentration, and this would account for the slight rise in the figures of the last columns in Tables I. and II.

As to the contention that the condensation of water and hydrogen chloride on the nuclei must occur simultaneously, the experiments indicated that a dry ammonium chloride mist (haze) would carry no free hydrogen chloride and hence it seemed fair to conclude that the absorption of water (it might be to some minimum extent) must precede the absorption of any hydrogen chloride. Subsequent to this the absorption of water and hydrogen chloride would no doubt go on simultaneously.

In reference to Dr. Coste's experiments with hydrochloric acid, it was perhaps of interest to record that in his (Professor Philip's) laboratory also it had been confirmed that strong hydrochloric acid did not fume in moist air, freed carefully from dust and ammonia.

SORPTION OF FOGS BY LIQUIDS.

By H. REMY (*from experiments with W. SEEMANN, A. PANCERAM and H. FRIEDLAND*).

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JAMES COLVIN.

The factors which influence the sorption of suspended matter on passage through liquids, filters or, even, empty vessels are, firstly, *sedimentation*, and, secondly, the collisions of the suspended particles with the walls or with the surrounding medium; the latter may be conditioned either by the individual movement of the particles (Brownian motion) or by the *turbulence* of the gas transporting them.

For suspended matter (such as the sulphuric acid fogs we have investigated), Brownian motion may be excluded at once as a decisive factor since, with particles of the diameter shown by this fog (10^{-4} cm.), it is far too slight relative to the observed decrease in concentration.¹ On the other hand various observations have been made which suggest that in such fogs sedimentation plays an essential part in the decrease in concentration on passing through the sorption apparatus; for example, damp fogs are less absorbed by solutions, the higher the concentration of the solution, and consequently the lower its vapour pressure;² again, the decrease in concentration of the fog in passing through a wash-bottle depends almost linearly on the reciprocal of the streaming velocity, *i.e.*

¹ Cp. H. Engelhard, *Z. Elektrochemie*, 1925, 31, 590.

² H. Remy and K. Ruhland, *Z. anorg. Chemie*, 1924, 139, 51; *cp. also* A. Winkel and G. Jander, *Schwebstoffe in Gasen*, p. 72 f. (Stuttgart, 1934)

on the time taken to traverse the wash-bottle.³ The experiments communicated here show, however, that this interpretation is not valid. Under experimental conditions such as we employ, sedimentation plays, at most, a quite subordinate part in the decrease in concentration of the fog. On the other hand, our experimental results are in complete agreement with the assumption that the essential factor is the turbulence of the transporting gas.

The experiments show that the dependence of the fall in concentration of the fog on the height of the layer of liquid through which it is bubbled is given accurately by assuming that the contact of the particles with the liquid depends solely on turbulence, and that sedimentation plays no part. The different sorptive action of solutions and pure water is therefore not to be attributed to an effect on the sedimentation velocity (as a consequence of reduction in the size of the particles by loss of water). Moreover, the dependence of the sorption on the streaming velocity in our experiments must be ascribed not to the influence which the time taken to pass through the sorption apparatus has on the amount of sedimentation, but to the dependence of the bubble size on the streaming velocity.

I. The Dependence of the Decrease in Concentration of the Fog on the Height of the Layer of Liquid through which it is Bubbled.

If a gas bubble carrying a fog rises with uniform velocity through a liquid, the number of particles coming into contact with the enclosing liquid as a consequence of turbulence within the bubble in the time interval dt (the time required to travel the distance ds) is proportional to the number of particles in unit volume. The concentration decrease in the fog is thus given by the equation:

$$-dc = a \cdot c \cdot ds,$$

where c is the concentration and a is a proportionality factor. Assuming uniform turbulence (by maintaining constant experimental conditions), the concentration decrease produced by traversing the interval s is

$$\int_{c_1}^{c_2} \frac{dc}{c} = \int_0^s a \cdot ds = -\ln \frac{c_2}{c_1} = a \cdot s.$$

$$(1a) \quad \frac{c_2}{c_1} = e^{-as}; \quad (1b) \quad c_1 - c_2 = c_1(1 - e^{-a \cdot s}).$$

The difference between the concentration, c_0 , of the fog on entering the sorption vessel and the concentration, c_s , on leaving was measured. This measured decrease in concentration consists of (1) the decrease $c_0 - c_1$, which the fog undergoes from the moment of entry to the moment at which it begins to rise with the gas bubble through the fluid, (2) the decrease $c_1 - c_2$, whilst it ascends through the liquid, and (3) the decrease $c_2 - c_s$, which ensues as the upper part of the sorption apparatus, where there is no liquid, is traversed.

$$c_0 - c_s = (c_0 - c_1) + (c_1 - c_2) + (c_2 - c_s) \quad . \quad . \quad . \quad (2)$$

If the experimental conditions, apart from the height of the column of fluid are kept constant, then

$$c_0 - c_1 = c_0 b_1, \quad c_2 - c_s = c_2 b_2,$$

³ H. Remy and C. Behre, *Kolloid Z.*, 1935, 71, 129; H. Remy and W. Seeman, *Kolloid Z.*, 1935, 72, 3.

where b_1 and b_2 are constants dependent on the experimental conditions. Substituting these in equation (2), and combining with equations (1a) and (1b), we obtain :

$$c_0 - c_s = c_0 \cdot b_1 + c_0(1 - b_1)(1 - e^{-as}) + c_0(1 - b_1)b_2 \cdot e^{-as}.$$

$$\frac{c_0 - c_s}{c_0} = 1 - e^{-as}(1 - b_1 - b_2 + b_1b_2)$$

$$-\ln\left(1 - \frac{c_0 - c_s}{c_0}\right) = as + \ln\left(\frac{1}{(1 - b_1)(1 - b_2)}\right).$$

Transforming from natural to common logarithms, and expressing the concentration decrease as a percentage of the initial concentration, we obtain

$$-\log\left(\frac{100 - A}{100}\right) = \alpha \cdot s + \beta, \quad (3)$$

where

$$A = \frac{c_0 - c_s}{c_0} \cdot 100.$$

Of the two coefficients, α is a measure of the absorption occurring during passage through the fluid, whilst β permits the calculation of the fall in concentration of the fog before and after this process.

Fig. 1 shows how accurately the linear dependence of the expression $-\log \frac{100 - A}{100}$ on the

height of the column of fluid, demanded by equation (3) is verified in our experiments using fogs of sulphuric acid, with water as the sorbent liquid. If sedimentation played a decisive part during the ascent of the bubble through the liquid, a curve should have been obtained, since in such clouds a substantial initial increase in the sedimentation velocity can be observed.⁴

A preliminary condition for good reproducibility of measurement is that the cloud should be produced under the same atmospheric pressure as that at which it enters the liquid, and that fluctuations of pressure during an experiment are carefully to be avoided.

Equation (3) permits the determination of the concentration decrease which the fog undergoes whilst bubbling through the liquid, from a few experiments carried out with different heights of liquid. It makes

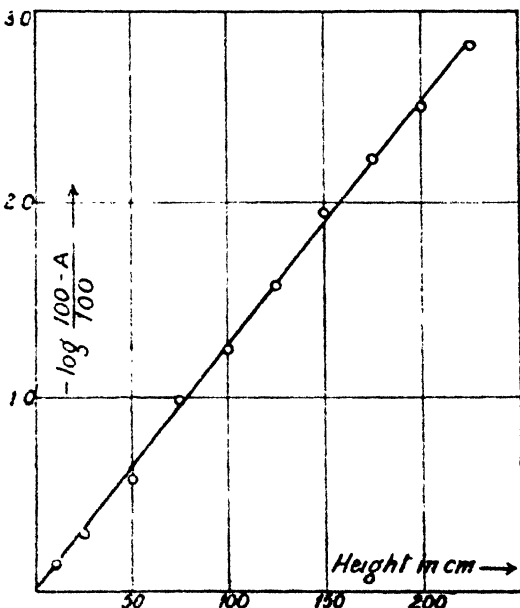


FIG. 1.—Dependence of the absorption of the fog on the height of the column of liquid through which it is bubbled.

⁴ H. Remy, *Z. anorg. Chemie*, 1924, 138, 167.

possible the elimination of the other concentration changes consequent on passing through the sorption apparatus. Theoretically, experiments with two different heights of liquid suffice, although in practice a larger number are employed in order to exclude chance errors.

In equation (3) α has the dimensions of reciprocal length. By multiplying $\frac{1}{\alpha}$ by $\log 2$, we obtain the height of liquid column required to reduce the fog concentration in the bubble to one half. In the experiments included in Fig. 1, this height was 24.0 cm. ($\alpha = 0.0125$, $\beta = 0.017$).

Similarly by varying the height of the space which the fog has to traverse after passing through the liquid to the outlet of the sorption apparatus, that part of the concentration decrease occurring there may be determined. In the experiments of Fig. 1 this height was 5 cm. For a liquid column (water) of 10 cm. (measured from the orifice of the inlet tube), A was found to be 27.90 per cent., of which 3.24 per cent. was due to the concentration decrease in the fog prior to its ascent through the liquid, 24.20 per cent. to the decrease during passage through the liquid and only 0.46 per cent. to the decrease in the part of the sorption apparatus not filled with liquid. With a liquid column of 25 cm. under

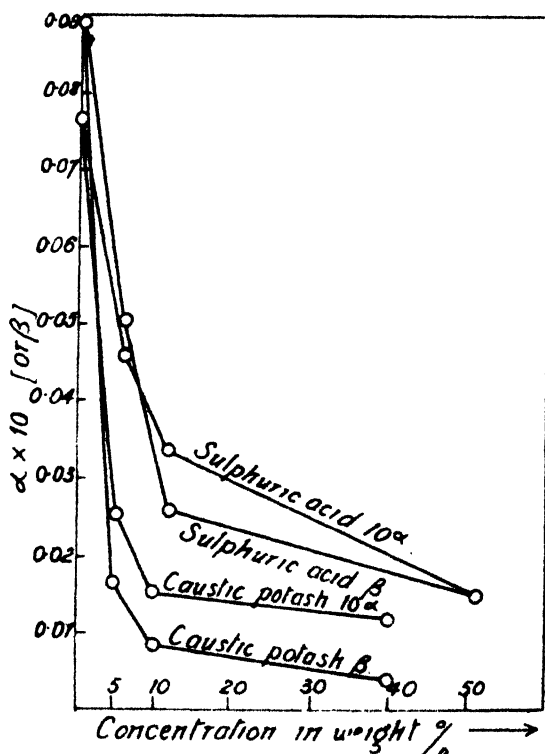


FIG 2.—Dependence of the absorption coefficients α and β on the concentration of the solutions used for absorption of the fog.

the fixed conditions, the concentration decrease above the liquid amounted to only 0.32 per cent. of the initial concentration in a total decrease of $A = 50.29$ per cent. The concentration decrease which the fog experienced between the times of leaving the liquid and escaping from the sorption apparatus was thus relatively slight, whereas that which occurs up to the moment at which single bubbles begin to rise through the liquid, is by no means negligible.

II. Sorption of Sulphuric Acid Fogs by Sulphuric Acid and by Caustic Potash Solution.

Our experiments have shown that equation (3) holds for both sulphuric acid and caustic potash solutions as absorption fluid, the co-

efficients α and β being affected in approximately the same way by the nature of the absorption fluid. This is shown by Fig. 2. Clearly, therefore, for the coefficient β , the decisive factor is the decrease in concentration of the fog which takes place, during the *time of formation of the individual bubbles* by absorption on the liquid boundaries.

Under the experimental conditions of Fig. 2, using pure water as absorption liquid, the coefficients had the values $\alpha = 0.0077$ and $\beta = 0.089$. Using 6.1 per cent. sulphuric acid, α fell to 0.0046 and β to 0.050. Using 5 per cent. caustic potash solution, $\alpha = 0.0025$ and $\beta = 0.016$. With further increase in concentration of the absorptive fluid, the rate of diminution of absorptive power fell off, as Fig. 2 shows. In Table I. are summarised the heights of the columns of liquid, by passing through which under the experimental conditions of Fig. 2 a fall in concentration of 50 per cent. is occasioned. (Half-value heights.) Thus 51 per cent. sulphuric acid possesses a five times smaller absorptive power, and 40 per cent. caustic potash solution, a $6\frac{1}{2}$ times smaller absorptive power than pure water.

TABLE I.—HALF-VALUE HEIGHTS OF DIFFERENT ABSORPTION FLUIDS.

Absorption Liquid.	Water.	Sulphuric Acid.			Caustic Potash.		
		6.1 Per Cent.	11.9 Per Cent.	51.25 Per Cent.	5 Per Cent.	10 Per Cent.	40 Per Cent.
Half-value height in cm.	39.1	66.1	89.4	202	119	196	257

The concentrations of the solutions in Table I. were so chosen that the sulphuric acid solutions and the caustic potash solutions had the same specific gravity. This was done in order to test whether solutions of the same specific gravity possess equal absorption coefficients; they do not, and there is just as little agreement in absorptive powers of solutions of sulphuric acid and caustic potash when compared at equal viscosity, equal surface tension or at equal vapour pressure.

III. Dependence of the Fog Absorption Coefficients on the Streaming Velocity of the Fog.

The results communicated in the two preceding sections were obtained using a streaming velocity of 0.2 litres per minute. The absorption fluids were contained in vertical glass tubes of 3.6 cm. width and of different lengths.

A second series of experiments was carried out at *different streaming velocities*, using Drechsel flasks as absorption vessels. Table II. clearly shows that α is dependent on the streaming velocity. It increases almost linearly with the reciprocal of the streaming velocity, *i.e.* with the reciprocal of the streaming velocity the bubble size decreasing⁵ correspondingly. The dependence of α on the streaming velocity is thus brought about by the fact that the size of the gas bubble in which the fog rises through the absorption liquid, is dependent on the streaming velocity. This cannot be ascribed to the fact that the amount of sedimentation of the fog is affected by changing the streaming velocity, since

⁵ H. Remy and W. Seemann, *Kolloid Z.*, 1935, **72**, 283.

in contrast to α , the coefficient β exhibits *no* such dependence on the streaming velocity, as would necessarily become apparent, if the concentration decrease were dependent to any real extent on sedimentation, since the time taken for the fog to pass through the sorption apparatus was varied ten-fold.

TABLE II.—THE ABSORPTION COEFFICIENTS α AND β AT DIFFERENT STREAMING VELOCITIES OF THE FOG.

Streaming Velocity in Litres Per Min.	0.1.	0.133.	0.2.	0.4.	1.0.
α	0.0301	0.0249	0.0192	0.0113	0.0076
β	0.04	0.05	0.02	0.04	0.04

The preceding statements support the view that the β -values are determined essentially by the concentration decrease of the fog before it bubbles through the liquid. The possibility of sedimentation after passage through the liquid was excluded in the experiments summarised in Table II., by keeping the empty space in the wash-bottle as small as possible (13 c.c.). If this small volume is exceeded to any considerable extent, sedimentation in this space may occur at low streaming velocities and affect the value of the sorption found under these conditions.

GENERAL DISCUSSION.

Mr. C. F. Goodeve (*London*) (*communicated*): Remy's attempt to distinguish between sedimentation on one hand, and Brownian motion and turbulence on the other, does not seem to have a very good basis. One usually considers that Brownian motion is quite distinct from the other two factors. If one increases the particle size and mass, the removal by sedimentation *and* by turbulence increases very rapidly, whereas the removal by Brownian motion decreases. If this fact is agreed, the conclusions that appear in the second and third paragraphs are not valid.

It does not seem to be very useful to choose the complicated conditions which arise in bubbling a fog through a liquid. This is borne out by the fact that Professor Remy's mathematical equations show that there is no agreement between the absorbing power and any one of the physical or chemical properties of the absorbing liquid. It would be much better to choose simpler conditions such as occur when one passes a fog over a liquid surface at known velocities under reproducible conditions. Experiments in an apparatus of this type are described in a later paper to this discussion by Dooley and the speaker.

Dr. N. Fuchs (*Moscow*) (*communicated*): I regret very much that I could not become enlightened personally as to the sense in which Remy uses the word "turbulence." It could hardly be used in the strict hydrodynamical sense, since within air-bubbles of some millimetres size the turbulent state could only be attained at such flow-velocities of the air as are practically impossible in the case considered. It seems therefore that Remy means by "turbulence" the irregular motion of the air within the bubbles which leads to continual intermixing, and to uniform distribution of the mist contained in them. If this is so, the exponential law of absorption of mists by liquid layers of different height found by Remy must hold good independently of the actual mechanism of the adsorption.

The intermixing of the mist cannot, however, by itself force the droplets to reach the walls of the bubble. For this the droplets must leave the

flow-lines of the air directed tangentially to the walls, which is possible under the action of three factors only (assuming the droplets are uncharged), viz., Brownian movement, gravity and centrifugal force. It seems that Remy has in view the latter. It is, however, easy to see that the effect due to centrifugal forces is small in comparison with sedimentation in the case considered here.

Near the walls of the bubble the droplets move under the action of centrifugal force with velocity $w = mvB/r$ where m and B are the mass and the mobility of the droplets, v velocity of air-flow in the bubbles, r their radius. The velocity of fall of the droplets is equal to mgB .

Assuming $r = 0.4$ cm. (the average size of air-bubbles in Remy's experiments) we come to the conclusion that both effects will be equal at $v = 20$ cm./sec. It is hardly possible to admit the existence of such flow-velocities within air-bubbles of such dimensions.

It seems, therefore, that sedimentation must play the chief rôle in the absorption of relatively coarse aerosols by liquids. It is, however, clear that sedimentation accompanied by continuous intermixing of the mist, now under consideration, is substantially different from sedimentation in still air, although the rate of settling at a given concentration of the mist should be practically equal in both cases. The only difference is that in the second case the rate of settling is constant (assuming the iso-dispersity of the mist and the absence of coagulation), and in the first it changes exponentially with time.

This conclusion could be verified quantitatively if the exact size of the droplets in the experiments of Remy were given. Assuming 1μ to be for the radius of droplets and 8 mm. for the diameter of the bubbles we can calculate that in 5 sec. about 20 per cent. of the mist will be absorbed owing to sedimentation.

Remy says later that if the absorption were caused by sedimentation of the mist then, according to his earlier experiments, there would be an acceleration of absorption during the rising of the bubbles. This statement seems to me not quite correct, since the time during which the bubbles move through the liquid in Remy's experiments¹ is so short (8 sec.) that there cannot be any perceptible coarsening of the mist.

Professor H. Remy (*Hamburg*), in reply, said: Removal by Brownian motion was excluded in my experiments by the particle size. The only possible causes of removal therefore, were sedimentation and turbulence. In the case of sedimentation we must distinguish between what happens during the rise of the bubble through the liquid and what happens in the liquid-free space of the absorption apparatus. The experiments described in the first and second paragraphs, exclude the influence of the latter effect; those in the third paragraph prove also that sedimentation within the bubbles has had no essential influence on the removal of particles since, with increasing of the streaming velocity, the times of formation of the bubbles decrease from 0.15 to 0.03 sec. The coefficient β in the experiments of the Table II. must therefore decrease considerably, if the removal of particles had been caused only by sedimentation, whereas, if turbulence had been the essential factor, β would be constant, because in this case the decrease caused by the shorter time would be paralysed by the increasing of the turbulence caused by the higher velocity of the air current. The word "turbulence" signifies the irregular motion of the air within the bubbles.

The "complicated" conditions of our experiments were given by the problems before us; we were not only studying the question discussed in this paper but a number of other questions, the results of which will soon be published in the *Kolloid Zeitschrift*.

It is true as Dr. Fuchs says, that my experiments do not decide what is the nature of the forces moving the particles through the air film in the

¹ Remy, *Kolloid. Z.*, 1935, 72, 285.

neighbourhood of the bubble wall ; as I have said in my paper, this question is as yet unsettled.

In the experiments of the first paragraph, the volume of bubbles was 0.48 c.cm., the initially falling velocity of the particles on entering the absorption apparatus was 3.5×10^{-3} cm./sec. If sedimentation only, without turbulence in the bubbles had taken place, the decrease of concentration in 8 secs. would have been 36 per cent., whilst 99.85 per cent. was found. According to earlier experiments,³ the falling velocity of the mist particles increases initially proportionally with time. Consequently, the decrease of concentration caused by sedimentation, must follow an equation of the form $-dc = (a_1 + a_2 t)c \cdot dt$, instead of $-dc = a \cdot c \cdot dt$. These questions will be discussed in the above-mentioned forthcoming papers.

³ H. Remy, *Z. anorg. Chemie*, 1924, **134**, 167.

FOG ALONG THE MEUSE VALLEY.

By J. FIRKET, Professor at the University of Liège.

Received 31st March, 1936.

From the 1st to 5th of December, 1930, a thick fog covered a large part of Belgium, along the Meuse (flowing from W.S.W. to E.N.E.), between Liège and Huy, about 15 miles above it. A large number of people were injured ; several hundred were severely attacked with respiratory troubles, and 63 died on the 4th and 5th December, after only a few hours of sickness. Many head of cattle had to be slaughtered. On the 6th of December the fog disappeared ; the respiratory troubles improved and, in general, rapidly ceased. Public opinion was deeply moved, not only in Belgium, but also in neighbouring countries. Wherever fogs of several days duration are frequent, public authorities were anxious to know the causes of this catastrophe and several delegates were sent to the spot. This apprehension was quite justified, when we think that, proportionally, the public services of London, *e.g.*, might be faced with the responsibility of 3200 sudden deaths if such a phenomenon occurred there.

A public enquiry was opened on 6th December and a group of five Liège University professors, Messrs. Dehalu, Schoofs, Mage, Batta and Firket, brought to this question their special knowledge of meteorology, toxicology, industrial chemistry and pathology. These experts had at their disposal the most complete means of investigation because the examining magistrate could require autopsies and have all doors and documents opened to him.

There follows an abstract of the objective statements and interpretations to which the experts came.

Medical Observations.—All the sick people felt a retrosternal pain spreading along the edge of the ribs ; they all had fits of coughing, dyspnoea of a paroxysmic and expiratory character such as asthma, or real polypnea, although the latter was less frequent.

Among those in whom asthma was particularly severe, or who previously had frequent asthmatic bronchitis, or even who had cardiac insufficiency or myocarditis, or again who received anti-asthmatic treatments too late, the respiratory troubles were complicated by cardio-vascular collapse, marked by a rapid pulse, pallor, cold extremities, profuse per-

spiration and sometimes, when it had been looked for, dilation of the heart. In the sick, whose respiratory troubles did not consist in attacks of asthma, but in quickening of the rhythm of breathing, cyanosis was observed, as well as a tendency to frothy sputum.

About fifteen autopsies with microscopical examinations of tissues and spectroscopical or spectrographical analyses of blood, and also toxicological analyses of all organs were performed. The histological examinations showed that noxious products had been inhaled in the last hours of life, and had brought on a local and superficial irritation of the mucous membrane of the respiratory ducts exposed to the air inhaled. The microscopical sections of the lungs showed, in addition, the inhalation of fine particles of soot even as far as the pulmonary alveoli.

It is to be noted that the first symptoms, shown by the first patients, began in the afternoon of the third day of fog, which had then been at its maximum opacity for several hours. On the other hand, on the 6th of December, when the fog dispersed, respiratory troubles grew rapidly better, so that death took place only on the fourth and fifth day of the fog. Moreover, the enquiry established that the first symptoms, marked by the first patients treated, were observed at the same time along the whole of the attacked region, i.e., for about 15 miles. It was thus impossible to discern the "diffusion" of a noxious gas in the atmosphere of the valley.

Meteorological Conditions.—The meteorological conditions existing from the 1st to 5th of December were as follows: Fog, starting on December 1st, anticyclonic conditions persisted, characterised by high atmospheric pressures and feeble wind, generally in an easterly direction, i.e., blowing upstream and slowly spreading smoke coming from the city of Liège and the large factories above it into the narrow valley. Moreover, a phenomenon of inversion of temperature established at about 90 yards from the soil a kind of atmospheric ceiling, lower than the hills bordering the valley and thus transformed the valley itself into a tunnel. The total volume of this tunnel could be approximately calculated therefore. Fine solid particles, mainly made of soot, had fallen during the five days of fog into the almost motionless atmosphere. Most of them—varying from 2 to 6 μ —must have taken two or three days to fall from the height of 40 to 70 yards, if we apply Stokes's law: 60 yards is the average height of the manufactory chimneys or the industrial region in question.

The conjunction of meteorological conditions observed in the beginning of December, 1930, is quite unusual in this district. During the last thirty years, fogs lasting more than three days have only occurred five times, always in winter (1901, 1911, 1917, 1919 and December, 1930). It is interesting to note that, because of the war, industry was not very active in 1917 and 1919, while in January, 1911, serious accidents occurred similar to those of 1930, but with attacks chiefly on cattle.

Chemical Analyses.—Since the fog itself could not be analysed, the chemists sought to ascertain the nature of the gas by analysis of deposits on the soil, but this was unsuccessful since they could not, in this way, distinguish the toxic substances which had been deposited only during the recent foggy period.

They established the balance of the gases which had polluted the atmosphere of the valley, by taking into account the activity of the factories of the region, as well as the number of domestic fires. For the factories, the raw materials used during the five days of fog and in many cases, intermediate products of gas and smoke were examined; very few results were available from the staffs of the factories. For the evaluation of domestic pollution, it was assumed that every house burned about 33 pounds of coal daily, the volatile sulphur in this being taken as about 1 per cent. The total number of houses was furnished by the local councils, so that approximate figures of SO_2 evolution could be arrived at; however, these figures must be considered as minima, since the basic figures of 33 pounds and 1 per cent. sulphur are relatively low.

The chemists succeeded in fixing, among about thirty substances found to be polluting the atmosphere, the maximum concentrations reached by carbon monoxide, carbon dioxide, nitrous gases, sulphur dioxide, hydrofluoric acid. They concluded that the SO_2 evolved in the presence of oxidation catalysts, such as ferric and zinc oxide, in the fog, the SO_2 must have been partly transformed in sulphuric acid.¹

The data thus collected and the toxicological analyses having been quite negative, the pathologists and industrial chemists sought to ascertain which of the thirty chemical substances left might have produced the medical symptoms described; only those had to be considered which cause irritation of the respiratory or other mucous membranes. They therefore excluded the lack of oxygen and carbon dioxide, carbon monoxide and divers solid dusts, the latter because of unsuitable anatomical observations. They also excluded a series of noxious gases which could not have reached their threshold of toxicity, according to the balance established previously by the chemists, or because they would have brought on other symptoms or lesions than those pathologically observed.²

Very few substances remained. They must have been either in a gaseous state, or dissolved in very fine liquid or solid particles which might have adsorbed toxic gases. Among such substances, maybe SO_2 and its products of oxidation, HF, nitrous or ammoniacal vapours, HCl. Cold and dense fog could not of itself bring about death within the limits of the time observed, since the fog was just as opaque over all the east of Belgium, and should have brought about similar accidents, but this was not the case.

Now, neither nitrous vapours, nor ammoniacal vapours, nor hydrochloric acid had existed in the atmosphere in sufficient quantity to produce the accidents observed along the entire extent of the unfortunate valley, at every part of it, and at the same moment. Again, hydrofluoric acid had been emitted by one single chimney, located about the middle of the region in question, but this could not be responsible, since no signs of its diffusion in the atmosphere were noted when taking records of the precise moment when the first patients felt their first symptoms all along the valley;

¹ The fifteenth annual report of the investigation of atmospheric pollution for the year ended 31st March, 1929, said (page 2): "A striking fact which emerged very early in the work was that in the place of experiment (Holborn) at all events, sulphur trioxide is not a normal constituent of the atmosphere; it appears only during fog." This result was at the time "somewhat unexpected," to the British observers who had been accustomed for fifteen years to analyse the atmosphere.

² The following examples will give an idea of the interpretation given by the experts concerning the calculations of industrial chemistry.

Consider the possibility of a lack of oxygen in the air of the valley, due to surcharge of the atmosphere with large amounts of gases of combustion during the foggy days. An approximate idea of the maximal amount reached by these gases of combustion in the valley is ascertained as follows. The total volume of the valley is estimated at 3×10^9 cubic metres (about 30 km. long, 1 km. wide and 100 m. high). If the gases of combustion had completely surcharged this atmosphere, none being diffused outside, they would not, according to the chemical balance, have exceeded the following maxima: 42×10^6 cubic metres for CO_2 , 10^6 for CO, 16×10^7 for nitrous gases, 10^5 for SO_2 , i.e., a total of 2031×10^6 cubic metres. The oxygen contained in the air of the valley would not have decreased by more than 10 per cent., i.e., it would still have constituted at least 19 per cent. of the atmosphere, whilst it was long ago proved by Haldane and Smith that life is perfectly possible in an atmosphere containing only 15 per cent. and even less of oxygen.

Again, if all the CO_2 had remained in the valley during the fog (supposing, as is unlikely, that no diffusion was possible) the maximum increase in CO_2 for the entire volume of the valley would be less than 1.5 per cent., whereas we know that man can live without discomfort in an atmosphere containing 2 per cent.

Moreover, the medical symptoms were not those usually observed in the case of need of oxygen, neither those of an intoxication by CO_2 .

it could not, however, be absolutely excluded as a secondary factor acting in the near neighbourhood of the factory which issued it.

There then remained only SO_2 , which issues in the largest abundance in the whole valley as a result of burning coal. It is moreover probable that part of the SO_2 (but it cannot be said, even approximately, how much) was oxidised into sulphuric acid, the threshold of toxicity of which is much lower. From the table, we can conclude that only the sulphur bodies have been spread in the whole valley, in amount sufficient to produce accidents among those exposed to the polluted atmosphere for several hours, while for all the other noxious gases, the amount established by calculation always remained far below the threshold of toxicity.

Sulphur dioxide probably existed in the air in amount insufficient to be noticed by its characteristic smell, but even in such small quantities, its toxicity for human beings may be very strong. It has been shown, e.g., by Lehman and Hess that amounts of SO_2 from 170 to 640 mgs. per cubic metre and dissipated after half an hour or even one hour may be fairly harmless, although even as little as 20 mgs. per cubic metre may cause serious trouble after several hours.

Moreover, only from the action of sulphur pollution can we explain

CALCULATIONS ESTABLISHED FOR 25 KMS. (about 15 MILES) of the VALLEY,
FROM HUY TO A POINT NEAR LIÉGE.

Name of Substance.	Rate of Toxicity after several Hours Exposure.	Maximum Amount which could have been reached after 1 Day of Fog.	Maximum Amount which could have been reached after 4 Days of Fog.
CO_2	2 per cent in volume	About 0.4 per cent. in volume	About $1\frac{1}{2}$ per cent. in volume
CO	$\frac{1}{2}$ f. 1000	About $\frac{1}{2}$ f. 1000	About $\frac{1}{2}$ f. 1000
NO_2	12 to 16 cgs. for 1 m. ³	1 to 2 mgs. f. 1 m. ³	4 to 8 mgs. for 1 m. ³
HF	Unknown; it must be about 4 mgs for 1 m. ³	0.08 mg. f. 1 m. ³	0.3 mg. f. 1 m. ³
SO_2	20 to 30 mgs. for 1 m. ³	25 mgs. f. 1 m. ³	100 mgs. f. 1 m. ³
H_2SO_4	4 mgs. f. 1 m. ³	36 mgs. f. 1 m. ³ (Supposing the whole	152 mgs. f. 1 m. ³ SO_2 would have been oxydated.)

why the accidents appeared simultaneously along the entire valley; several hours of breathing such an atmosphere, where the noxious gases existed in relatively low amount, were necessary to provoke respiratory troubles. Several hours were also needed before the lower parts of the atmosphere, near the soil, were charged with sufficient quantities of sulphur bodies (mainly adsorbed on sooty particles; the latter, issued from the high factory chimneys, could only reach the soil after several days). Moreover, a certain time had to elapse before the oxidation factors transforming SO_2 into SO_3 could act.

From the pathological standpoint, the two types of respiratory troubles noticed favour to a certain extent the idea that the noxious gases were sulphur dioxide and sulphuric acid. The physicians of the valley had all noticed, during the foggy days, (a) symptoms due to direct irritation of the mucous membranes with reflex symptoms (asthma and subsequent vascular collapse), certainly caused by a state of alkalosis in the blood, (b) on the other hand, symptoms of polypnaea with edema of the lungs, i.e., action of noxious gases on the wall of pulmonary alveoli and very probably anoxaemia with acidosis of the blood. It is now well known² that irritant gases are

² Especially after the research of Henderson and Haggard.

mainly of two types according to the region of the respiratory ducts where they act: the soluble and dense vapours like H_2SO_4 in fine droplets will be fixed by the superior respiratory ducts, trachea or bronchi, while the lighter and less soluble gases, i.e., SO_2 will penetrate into the deep cavities of the lungs and produce edema: in the first case, the clinical symptoms will be those of asthma; in the second, those of anoxaemia with acidosis.

Finally, from the geographical distribution of the gravely attacked patients and the dead, one could see that the rate of SO_2 was higher at the extremity of the valley near Liège where factories and private houses are more numerous, than at the other end near Huy. The geographical conditions of the valley above Liège are really very unusual and unfavourable when a weak easterly wind and fog appear together.⁴

In conclusion, we believe that undoubtedly the conjunction during more than three days of the same exceptional meteorological conditions would cause the same accidents if the industrial and domestic fires are equally active. Our measurements led us to the idea that one-fifth of the SO_2 issued in the valley came from domestic fires. Moreover, chemical analyses to control the pollution of the atmosphere in Liège itself (especially of sulphur bodies), showed that the latter reached a level in the city ten times higher than thirty years ago. The problems and the catastrophe here studied demonstrate once more the social and hygienic importance of questions connected with atmospheric pollution. In that field Great Britain is really the leading country.

Liège, 27th March.

⁴The extensive report of the question here summarised can be found in pages 260-335 of *Les problèmes de pollution de l'atmosphère*, by G. Batta, J. Firket and E. Leclerc. Edit. Georges Thone, Liège, and G. Masson, Paris, 1933 (462 pages).

GENERAL DISCUSSION.

Professor Firket in introducing his paper, referred to a scale map of the Meuse valley.

Mr. J. H. Coste (*Teddington*) said: The concentrations of sulphur compounds suggested by Firket as possible in the air of the Meuse valley during the fog in question are much greater than we have found in London under any weather conditions. Most people, it is supposed, can smell SO_2 when its concentration reaches 2 volumes per million, but it seems probable that sensitivity varies very much according to customary exposure; a member of my family who has never lived in a large town can smell SO_2 in the white to pale yellow fogs we get in the semi-rural parts of the Thames valley, whilst town dwellers are probably less sensitive.

It seems probable that during bad fogs in industrial or crowded districts sulphuric acid is present in irritating amounts. In the fog of 23rd December, 1935, mentioned in my paper, the air, especially around the period of high SO_2 concentration was very irritant, affecting both the respiratory passages and the thin skin around the eyes. The effect was not unlike one's sensation when evaporating sulphuric acid in small quantities in a room.

In an industrial district there would always be enough nitrous acid in the air in still weather for appreciable oxidation of SO_2 to occur.

The evidence collected by the commission, which I read when the report was issued, was mainly circumstantial, but I think that an unusually big formation, with little dissipation, of sulphuric acid, was the most probable cause.

Dr. F. J. W. Whipple (*London*) said: The meteorological conditions described in Firket's paper are puzzling. It appears that there was

measurable wind throughout the period, and this seems at first sight inconsistent with the hypothesis that the air was practically stagnant in the valley. However, Firket has not given any information about the height of the Observatory where the wind was recorded, and it may be that the air current was persistent above the fog, which was confined to the valley. With a sharp inversion of temperature the upper air could glide over the top of the fog without dragging it along. It is perhaps important to notice that in a fog which is being cooled by radiation from the top and warmed by contact with the ground there is gentle convection and the temperature is nearly uniform. It is not justifiable to assume that smoke particles merely settle down through the fog, they are carried down by the convection currents.

It is difficult to believe that the deaths were due to breathing sulphur dioxide, since the conditions in the valley could hardly have been so bad as those which prevailed in the tunnels of the underground railway in London in the days of steam trains, where the sulphurous fumes were notorious, but conditions were not found unhealthy by the railwaymen. Is it not possible that some noxious product of the furnaces in the Meuse Valley has been overlooked?

Dr. R. Lessing (*London*) said that he had directed attention to the emission of sulphur oxides in the combustion of fuels ¹ six months before the Meuse tragedy. In a later paper, ² he had shown that the annual emission of sulphur oxides in Greater London was, at a low estimate 500,000 tons in terms of H_2SO_4 . The reason why free SO_2 or sulphuric acid was so rarely observed in the atmosphere was that it was readily neutralised by the lime or other basic dust always present in town air. During the first two or three days of the Meuse fog the lime particles settled out along with the soot and other solids so that later the sulphuric acid could not find neutralising material to act upon. Moreover, the high moisture saturation provided an ideal medium for the oxidation of SO_2 to SO_3 at a higher rate than in dry air.

Mr. G. Nonhebel (*Billingham*) (*communicated*): The statements by Professor Firket that 20-30 mg. SO_2/M^3 and 4 mg. SO_3/M^3 air may cause trouble after several hours leads to the question: "What are the safe upper limits for the SO_2 and SO_3 concentrations in the lee of a large modern power station burning coal at a peak rate of several thousand tons per day." We have found that up to 10 per cent. of the sulphur in the gases from a powdered fuel plant may be present as SO_3 .

Dr. S. R. Carter (*Birmingham*) said: Although excessive fog in the Meuse Valley is the subject under discussion, the reverse question interests me, as on the occasions when I have visited Liège the atmosphere seemed to be remarkably clear considering that it is a large manufacturing town. Is the reason for this known?

¹ Second World Power Conference, Berlin, 1930.

² The National Smoke Abatement Conference, Bristol, 1935.

SULPHURIC ACID AS A DISPERSE PHASE IN TOWN AIR.

By J. H. COSTE AND G. B. COURTIER.

Received 10th January, 1936.

The sulphur in air is mainly present as sulphur dioxide but under some atmospheric conditions it has been found that air from which the sulphur dioxide has been removed still shows measurable sulphur acidity. The acid constituent can be retained on a suitably fine filter, but experiments made with asbestos, sintered glass, and cotton wool filters confirmed our opinion that methods involving such filters are unsuitable when the acidity is of the low order found in the atmosphere. Apart from the small possibility that the filtering material may itself yield on extraction either alkali or acid to water, it is likely to separate from air all but the very finest suspended matter. This may, and probably does, include all or almost all the acid which is present in other forms than gas or vapour, but it will in most cases include particles which are either basic and when treated with water will yield a liquid of p_H greater than 7, or will easily be attacked by strong acids with the liberation of weaker ones, e.g., carbonic or silicic acids.

We have, therefore, sought a means of separating free sulphuric acid from the air in which it may be present, without mixing it with the many other matters held in suspension in air. Since sulphuric acid is a very hygroscopic substance we have sought to take advantage of this fact by inducing condensation of water vapour by cooling, which should increase the mass of droplets of sulphuric acid or other hygroscopic nuclei so as to enable them to fall to the bottom of a vessel.

Experimental Methods.

Air which had been freed from sulphur dioxide was almost saturated with water vapour at room temperature and then passed through a flask immersed in ice. A condensate representing the greater part of the water content was obtained, which when sulphuric acid was found to be present, would have formed on nuclei of that compound in droplets sufficiently large to be retained in the flask. The condensate was almost free from dust and smoke particles, which passed through the flask and could be retained on a filter.

About 1000 litres of air were passed during 24 hours, yielding between 5 and 10 ml. of condensate. The p_H value was measured in the absence of carbon dioxide, and samples showing appreciable acidity were titrated with $N/250$ potash from a micro-burette using purified distilled water as the blank. In order to detect the presence of sulphates, 1 ml. of the condensate together with a drop of barium chloride solution was transferred to a watch glass and allowed to evaporate slowly on an electrically heated plate. Crystals of barium sulphate were observed, giving definite proof of sulphates in all samples showing acidity. Comparison with dilute standard solutions of sulphuric acid precipitated under the same conditions indicated that the acidity of the condensates could be attributed to sulphuric acid.

In the first experiments the compound of hydrogen peroxide and urea (Hyperol) was used for the absorption of sulphur dioxide. Hyperol is

more stable than free hydrogen peroxide in dilute solution and has a lower vapour pressure. Using a solution of about 1 per cent. in purified water and with two gas washers in series, it has been found, from extensive experience of sulphur determinations in air, that not less than 99 per cent. of the total absorption takes place in the first washer. Since this is true for the whole range of concentrations encountered, it can be assumed that with two washers gaseous absorption is virtually complete. Air passed through these washers yielded, on cooling, condensates with p_H values varying in different samples between 4.3 and 5.6. It was thought that there might be some possibility of sulphur dioxide being oxidised by hydrogen peroxide vapour in the gas phase with the formation of sulphuric acid, which would pass through the washers unabsorbed, and when deposited by water condensation might be considered as having been present in the air originally. Some further tests were therefore made using a solid absorbent having no appreciable vapour pressure. Broken pumice coated with lead peroxide, in U tubes, was found to be very efficient for the purpose, as air which had passed through these tubes yielded no acid to hyperol solution. When using lead peroxide for the preliminary removal of sulphur dioxide, the water vapour content of the air was raised nearly to saturation by passage through a wash tube, and when condensation was induced by cooling the water formed was found to be slightly acid as in the previous tests. The condensates obtained under these conditions had p_H values between 4.8 and 6.0. These values were rather higher than in the first series of tests but the difference can be attributed, at least in part, to the filtering action of the closely packed tubes.* Further evidence that the presence of sulphuric acid was independent of oxidation in the reaction tubes was obtained after using potassium hydroxide solution for the absorption of sulphur dioxide. A tube of pumice chips was inserted to prevent the passage of spray, and a p_H of 5.0 was measured.

A sensitive test for sulphurous acid is the change in blue shade produced in water slightly coloured by starch-iodine. When the condensates obtained by the above methods were tested with this reagent there was no evidence of the presence of sulphurous acid, although this was readily detected in samples resulting from the direct cooling of air without previous removal of sulphur dioxide. It was established that oxidation in such solutions was not rapid, and the absence of sulphurous acid in the condensates confirmed that the methods for preliminary removal of sulphur dioxide were adequate.

The "Monax" glass used for the apparatus, when thoroughly cleaned, was not appreciably affected by the solvent action of cold water having a p_H of the order encountered during the experiments.

Results.

The experiments were made, mainly in central London, under a variety of atmospheric conditions. The qualitative tests of the condensates obtained by the above methods consistently indicated the presence of traces of sulphuric acid, and the amounts were estimated to vary between 1 and 20×10^{-6} gm. per 1000 litres; the sulphur dioxide in the same samples of air varying between 0.10 and 0.50 ml. (equivalent to 440 and 2200×10^{-6} gm. sulphuric acid). The maximum amounts of sulphuric acid were usually registered in periods of calm and in foggy conditions, while the amounts were invariably small after rain. No exact relationship was established but, in general, conditions which favoured high sulphur dioxide content also favoured high sulphuric acid content. There was some evidence that

* After the above was written, Mr. H. L. Wright found, in the course of further work with one of us on the nature of hygroscopic nuclei, that similar tubes packed with lead peroxide allowed only from 1/9 to 1/5 of the nuclei originally present in air to pass through, whilst the reduction in number of nuclei when air was passed through hyperol was of the order of 10 per cent.

the proportion of sulphuric acid was greater at ground level than at sixth floor level. Some observations made at an outlying northerly suburb showed that while the sulphur dioxide content was only 0.02 ml. per 1000 litres (equivalent to 44×10^{-6} gm. sulphuric acid) the amount of actual sulphuric acid was 4×10^{-6} gm.

From the experimental methods employed it may be concluded that the failure to retain the acid in the earlier absorbers with the gaseous sulphur dioxide was due to the existence of the sulphuric acid, probably associated with water, in aggregates of molecules—hygroscopic nuclei. Although the extraction of sulphuric acid in the condenser was not entirely complete, as was shown by the addition of an extra saturator and condenser, it did not appear that the total acid content was much greater than that stated.

Discussion.

The presence of such very small proportions of sulphuric acid in air containing relatively large proportions of sulphur dioxide may be explained on other grounds than the slowness of oxidation of the dioxide. When it is considered that facts point to the most obvious oxidising agent—nitrous acid—as occurring in air mainly in a liquid, or at least non-gaseous, phase,^{1, 2} it appears that oxidation must be rather slow.

Sulphuric acid, as formed, will rapidly pass almost entirely into a liquid phase, although action occurring between sulphuric acid and a steam jet near which a drop of the strong acid is brought can only be explained by the concentrated acid having an appreciable vapour tension.³

N. Fuchs and N. Oschman⁴ in attempting to form stable aerosols of sulphuric acid found difficulty in overcoming the tendency of droplets to combine to form larger ones. They succeeded, however, by rapid dilution of concentrated aerosols with relatively dry air, in obtaining uniform aerosols containing droplets estimated at 1.5×10^{-6} cm. radius in relatively dry air, which is of the same order as that of the nuclei of Aitken⁵ and the large ions of Langerin, which are considered as charged nuclei. A million of these per ml. of air would yield concentrations of H_2SO_4 of the order we have found. One of us and Wright² found that the rate of disappearance of nuclei obtained by burning fuel containing sulphur or by projecting SO_3 into air was very rapid, and this may be due as much to growth by absorption of water until the droplets are large enough to fall through the air with an appreciable velocity, as to recombination, although both these actions must go on. The tendency to form ammonium sulphate (ammonia is usually present in air), coalescence with heavy particles, including calcium carbonate (from building materials) and coke, must not be overlooked. Dusts collected in inhabited or industrial districts contain both alkaline and acid particles, these latter frequently being coke with an acid surface film, as shown under the microscope by the use of indicators. Frequently they contain sulphate.

The facts, generally, show that a considerable liquid phase of sulphuric acid droplets is very unlikely to occur in air; the conclusions,

¹ A. G. Francis and A. T. Parsons, *Analyst*, 1925, **50**, 262-72; G. Defren, *Chem. News*, 1896, **74**, 230-1, 240, 241; W. Hayhurst and J. V. Pring, *Trans. C. S.*, 1910, **97**, 868-77.

² J. H. Coste and H. L. Wright, *Phil. Mag.*, 1935, Sec. 7.20, 209-34.

³ R. V. Helmholtz, *Ann. Physik u. Chem.*, 1887, **32**, 1-19.

⁴ *Acta Physicochimica U.R.S.S.*, 1935, **3**, 61-78.

⁵ J. J. and G. P. Thomson, *Conduction of Electricity through Gases*, 1928, 187-9.

based, it must be admitted, on circumstantial evidence of the Commission which reported on the Meuse Valley fog of 1st to 5th December, 1930, raise the strong presumption that when sulphuric acid becomes an important constituent of fog catastrophic disaster may be expected.

Summary.

A method of investigating the sulphuric acid content of the air has been devised, which does not involve the use of filters. The free sulphuric acid content of London air has been shown to be of the order of 1 to 20×10^{-8} gm. per cubic metre.

This is of the order which would be expected having regard to the numbers of Aitken nuclei and the mass of sulphuric nuclei in artificially prepared aerosols of this acid.

*Chemical Laboratory of the
London County Council.*

^{*} *Bull. Acad. Roy. Med. Belg.*, 1931, 683-732.

GENERAL DISCUSSION.

Mr. C. F. Goodeve (*London*) expressed incomplete agreement with Coste and Courtier in the usefulness of the apparatus they described, and he did not agree that sintered glass filters are unsuitable.¹ Such filters have been used to test the amount of sulphuric acid, in excess of the alkalinity, present in London's atmosphere on a number of occasions during January and February, 1934. The extreme simplicity of the filter method over any other method makes it well worth considering carefully from the point of view of routine observations. On the other hand the apparatus described by the authors requires careful watching and is slow with regard to the amount of air handled per hour.

It is agreed that the two methods might give slightly different results, but only if acid and alkaline particles exist independently in the atmosphere. There is no evidence at present to show whether or not this is the case, but the argument given in the paragraph below leads to the conclusion that it is unlikely.

Even if it is considered that the two methods do give different results, those obtained by the filter method would appear to have important practical advantages over those obtained by the method described by the authors. The importance of knowing the sulphuric acid content of the air is largely due to its action on building materials and on living tissues. This action will be partly offset by the alkaline particles and therefore the *net* acidity is of importance.

The speaker called attention to the important observations of Ellis² who found that, even in the presence of high concentrations of a sulphur dioxide, the sulphuric acid content of London air was immeasurable, except in the presence of fog. They found a maximum value of 0.62 volume parts per million (calculated as SO₂). Some of the values obtained at University College during February, 1934, are shown in the table on next page.

The absence of sulphuric acid before fog particles are formed indicates that it cannot be considered as a *cause* of fog formation but rather as a contributing factor to the intensification of fog. The amount of sulphuric

¹ The use of the sintered glass filters is discussed later, p. 1220.

² *The Investigation of Atmospheric Pollution*, Report on Observations, 1931, p. 38.

Date.	Volume of Air litres.	Time. Hours.	H ₂ SO ₄ p.p.m. (vol.).	Remarks.
12/2/34	3440	7½	0.034	Slightly foggy.
14/2/34	2360	9½	0.019	Less " "
15/2/34	3660	9½	0.015	" " "
16/2/34	3580	9½	0.009	Fog in morning.
23/2/34	1390	7	0.0	Clear.

acid formed in flue gas is very small and the rate of oxidation in sulphur dioxide gas in the absence of liquid water is also small. Dr. Pinck (unpublished results) found that there was no oxidation in the presence of dry catalysts, such as iron oxides, even after a considerable period of time, but when water vapour was present sufficient to produce an adsorbed film over the catalyst, rapid oxidation at once took place. The formation of sulphuric acid in the atmosphere can take place by the condensation of water on nuclei (either alkaline or neutral), the subsequent solution of sulphur dioxide, and its rapid oxidation catalysed by the solid nuclei. If this is the case, there is no reason for the existence of independent alkaline particles in fogs and the two methods of analysis discussed above should give the same result.

Mr. J. H. Coste (*Teddington*), in reply, said: It is true, as pointed out by Mr. Goodeve that sintered glass is a good filtering medium for removal of dispersoids from air. In considering the useful work of Ellis (who used an asbestos filter as suggested to the Research Committee by Lambert of Oxford) I feel in the light of the certainty that acid and alkaline particles do exist together in air (a fact that Mr. Goodeve seems to doubt), that any method in which all the dispersoids are collected together is likely to yield erroneous results. Mr. Nonhebel has found that up to 10 per cent. of the sulphur in the gases from a powdered fuel plant may be present as SO₃, the amount of accompanying water vapour being great. This would go into the air as droplets, which would only be neutralised by collisions with alkaline particles or absorption of ammonia. Again, any sulphuric acid formed by the action of nitrous acid would be in droplet form, and neutralisation in free air would be much slower and less likely than when air was forced through a filter which was also separating alkaline particles.

The offsetting effect of alkaline particles can only come into play if acid and alkali are in juxtaposition. In collections of rainwater, containing the solids brought down with it, I have found alkaline zones surrounding particles in an acid liquid; thus neutralisation does not always happen.

Mr. Goodeve's observations on fog are very interesting, and I agree with him that the presence of abundance of droplets of water with an accumulation of sulphur dioxide (and nitrous acid) which would occur in a town fog is likely to raise the sulphuric acid content from an infinitesimal to a measurable amount.

THE INFLUENCE OF URBAN CONDITIONS ON THE CIRCULATION OF ELECTRICITY THROUGH THE ATMOSPHERE.

BY F. J. W. WHIPPLE.

Received 30th March, 1936.

Atmospheric electricity is a subject in which it is difficult to disentangle the influence of world-wide forces and of local conditions. In every situation there are a number of phenomena to be observed and correlated, and at present there is no observatory which can claim that all the relevant measurements are being made regularly, or even intermittently. Of the elements which can be recorded, potential gradient is by far the most frequently observed, but the interpretation of the changes in the value of this element is now known to be very complicated.

It has been realised for a long while that the fact that there is a gradient of potential is evidence for the existence of a charge on the ground, and of a complementary charge in the atmosphere. Normally the ground carries a negative charge, and the complementary charge is positive. Observations in balloons indicate that the potential gradient falls off rapidly with increasing height, so that the charge in the atmosphere is mostly at low levels. One way of regarding observations of potential gradient is that they are measurements of the space-charge in columns of the atmosphere.

Alternatively, attention may be concentrated on the flow of electricity. Owing to ionisation, the air is a conductor, and under the influence of potential gradient a current flows from the upper air to the ground. In a steady state the current must be the same at all heights. This rule is in accordance with observation, *i.e.* in individual ascents the product of potential gradient and conductivity has been found to be constant, as nearly as can be expected from the circumstances of the observations.

A fundamental problem in Atmospheric Electricity is to explain how this air-earth current, which prevails in fine weather in all parts of the world, is maintained. It is known that in the upper atmosphere there are layers of highly ionised air, of which the most important from the present point of view is the Kennelly-Heaviside layer at a height of about 100 km. The conductivity of this layer is so good that it must be at very nearly the same potential over all parts of the world.

If electricity flows downwards from the Kennelly-Heaviside layer in regions where there is fine weather, the supply must be maintained by upward currents predominating in regions where there is bad weather.

In fact, rain-clouds act as electrical machines pumping electricity up towards the K.-H. layer. Wormell has shown that the available estimates of the quantity of electricity exchanged between clouds and ground by conduction currents, by charged rain and by lightning are consistent with this hypothesis, which, it may be noted, does not involve any particular theory of the mechanism by which the separation of electricity in the clouds is produced.

The potential of the K.-H. layer being the same in all parts of the

globe, the current which flows towards the ground in any place must depend on the conductivity of the air, the current varying inversely as the effective resistance of the column of air between the ground and the Heaviside layer. The electricity is carried by ions, positive ions moving downwards and negative ions upwards; it is only by the current of positive ions that electricity is communicated to the ground, so that the strength of the air-earth current is proportional to the potential gradient and to the conductivity due to positive ions. This may be expressed otherwise by saying that the potential gradient is proportional to the current, and to the specific resistance of the air.

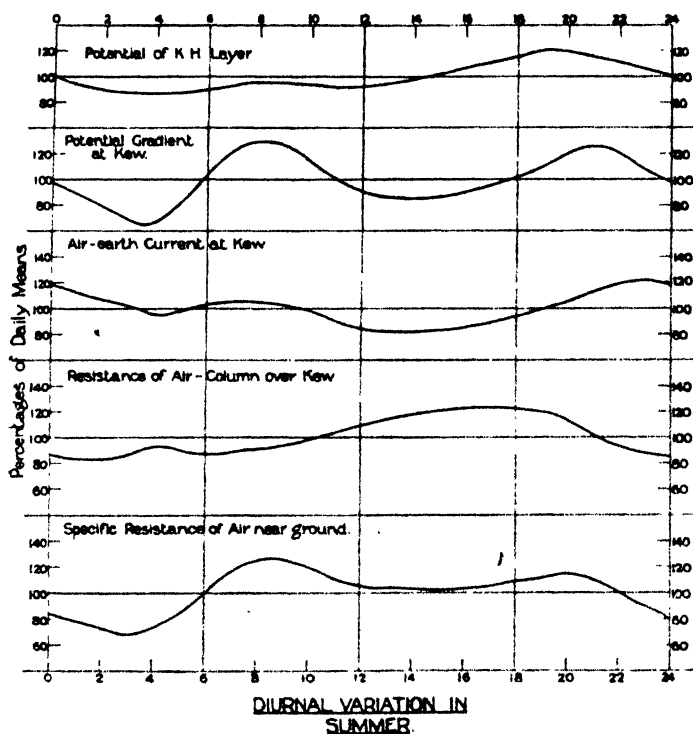


FIG. 1.

It will be seen that, according to the theory which has been sketched, the potential gradient at any time and place is

- (a) proportional to the potential of the K.-H. layer;
- (b) inversely proportional to the effective resistance of a column of the atmosphere;
- (c) proportional to the specific resistance of the air near the ground for positive electricity.

It is proposed to apply this theory to the interpretation of observations of the diurnal variation of potential gradient at Kew Observatory. For this purpose, we shall consider the diurnal variation during four summer months and four winter months in 1930 and 1931, during which there were continuous records¹ of the air-earth current at the Observatory.

¹ F. J. Scrase, "The Air-earth Current at Kew Observatory," *London Met. Office Geophysical Memoirs*, No. 58 (1933).

Fortunately, these short periods yielded diurnal variation curves which were true to type. These are shown in the second lines of Figs. 1 and 2. Both in summer and in winter there are two maxima and two minima in the course of the day.

The uppermost curves in the diagrams represent the diurnal variation of the potential of the Heaviside layer. These curves are not as speculative as might be supposed. It will be noticed that the absolute value of the potential is not involved, we are only concerned for the moment with proportional changes. Now, it will be realised that over the oceans there is no pollution, and no considerable systematic variation in temperature, so it may be assumed that at points far from land the total resistance of a column of the atmosphere is constant throughout the day,

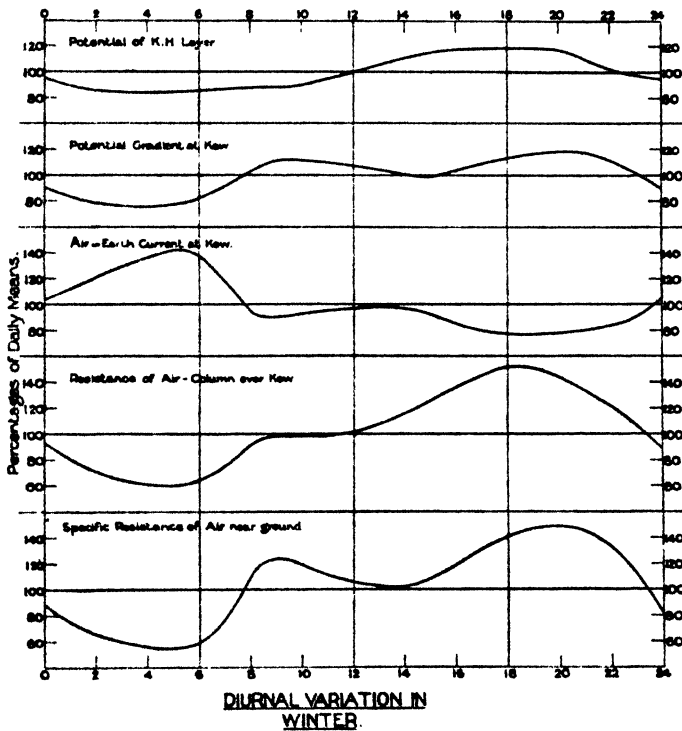


FIG. 2.

and also the specific resistance of the air in the lowest layer. Accordingly, the changes in potential gradient are proportional to the changes in the potential of the Heaviside layer. Now, it was established by Mauchly that the changes in potential gradient over the oceans depended on Greenwich time, not local time, and this is confirmation of our hypothesis. The curves to which reference has been made are derived² from the observations of potential gradient over the oceans; the curve used for comparison with the Kew potential gradient on summer depends on observations during the months May to October, and that for comparison with the Kew gradient in winter on observations during the

² Whipple, *Q.J.R. Met. Soc.*, 1929, 55, 9.

months November to April but the difference in type is slight, so that no serious error can be introduced by this selection of months.

The curves indicate that the potential of the K.-H. layer is lowest about 4 h. G.M.T., and highest about 19 h. G.M.T. As was first noticed by Appleton, this is consistent with the ideas that the potential is maintained by the action of thunderstorms, that in any place on land thunderstorms are most likely in the late afternoon, and that the most thundery regions are in Africa and South America.

The next step is to consider the observations of the air-earth current at Kew. As will be seen from the curves in Figs. 1 and 2, the types of variation of the current in summer and winter are very different. In summer the current behaves in much the same way as the potential gradient at the same station, in winter there is a reversal.

Regarding the current as produced by the potential of the K.-H. layer, we investigate the changes in the resistance of a vertical column by dividing the potential by the current. We learn in this way that the resistance is least in the early morning, and increases fairly steadily through the day, the maximum being reached about 18 h.

The specific resistance of the air in contact with the ground is found in the same way by comparing the potential gradient at Kew with the air-earth current. The specific resistance has two maxima and two minima in the twenty-four hours.

Thus it appears that the morning minimum and the evening maximum of potential gradient at Kew are due in part to the corresponding extremes of the potential of the K.-H. layer, but the morning maximum and the evening minimum are due entirely to local conditions.

At the time of the morning maximum of potential gradient the specific resistance near the ground is high, whilst the total resistance is low (in summer) or moderate (in winter). At the time of the afternoon minimum of potential gradient the specific resistance is moderate, whilst the total resistance is above the mean for the day. To explain the variations in the total resistance, we notice that the conductivity of the air depends on the number of small ions which it contains. The number of small ions depends on the rate at which ions are produced, and on the rate at which the lives of the small ions are terminated by their combination with nuclei, charged and uncharged. We do not know whether the rate of production fluctuates through the day at moderate heights in the atmosphere, but we do know that the number of nuclei will increase owing to the way they are steadily produced by fires and by the use of gas. According to the work³ of Coste and Wright, nuclei are mostly nitrous acid HNO_2 , formed by the combination of the atmospheric gases nitrogen, oxygen and water vapour and therefore nuclei can hardly be regarded as pollution. They are produced, however, at the same time as the sooty particles which are pre-eminently pollution. The way in which the total resistance changes indicates that over a London suburb the number of nuclei increases steadily from the time when fires are lit in the morning until about 18 h. in the evening, and that the air clears gradually during the night. It is probable that at night in summer the nuclei are mostly sea-salt, as they are at all times over the oceans.

The double oscillation in the specific resistance of the air near the ground has been explained by Simpson. There is a rapid increase in the

³ *Phil. Mag.*, 1935, 7, 20, 209.

resistance in the morning, but this increase is interrupted when the sun is up and the warming of the ground produces convection currents which carry pollution and nuclei upwards and allow purer air to descend. Convection becomes less vigorous in the late afternoon, and pollution increases to reach a maximum in the evening when domestic fires and domestic cooking-stoves are still active. The evening maximum is a little later in winter than in summer.

In this discussion we have dealt only with the proportional variation of the elements concerned. In considering the mean values, we are handicapped by not knowing at all precisely the mean value of the potential of the Heaviside layer at different seasons. There is reason to believe that the potential is higher in the northern winter than in the northern summer, for it is found both in the Arctic and in the Antarctic that potential gradient is higher in the former season, and the same relation has been observed over the oceans. On the other hand Mauchly's final analysis⁴ of the Carnegie observations of potential gradient indicates no appreciable annual variation over the oceans. Balloon observations of potential gradient lead to an estimate of about 2.5×10^5 volts for potential at 10 km. Above that level the gradient is very small. We take 3×10^5 volts for the potential of the Heaviside layer at all seasons.

The best estimate of the air-earth current over the oceans can be obtained from the mean potential gradient and the conductivity due to position ions and is

$$1.3 \times 1.8 \times 10^{-16} = 2.3 \times 10^{-16} \text{ amp./cm}^2.$$

The following Table is completed⁵ by taking Scrase's estimates of the potential gradient and air-earth current at Kew.

MEAN VALUES.

	Oceans.	Kew Observatory.	
		Summer.	Winter.
Potential of the Heaviside layer	3	3	3×10^5 volts.
Potential gradient . . .	1.3	2.46	4.70 volt/cm.
Air-earth current . . .	2.3	1.48	$.74 \times 10^{-16}$ amp./cm. ²
Effective resistance of air column	1.3	2.0	4.0×10^{11} ohm.cm. ²
Specific resistance (+ ions) .	0.56	1.66	6.35×10^{10} ohm.cm.
Conductivity (+ ions) . . .	1.8	.60	$.16 \times 10^{-10}$ ohm. ⁻¹ cm. ⁻¹
Conductivity in electrostatic units	1.6	.54	$.14 \times 10^{-4}$ sec. ⁻¹

It will be noticed that whereas the specific resistance at Kew is increased fourfold between summer and winter, the total resistance of the air-column is only doubled.

The minimum resistance, at 5 h., in winter, is nearly equal to the maximum resistance, at 18 h., in summer. Further, the winter maximum,

⁴ *Carnegie Inst. Dep. Terr. Magn., Washington, 1926, 8, 403.*

⁵ *Loc. cit.* Tables IV. and II. It is to be noted that an exposure factor has to be applied to the data in these Tables. The conductivity is derived here from seasonal means of current and potential gradient, whereas in Scrase's Table III. the values of conductivity for the months were averaged.

at 19 h., is about 6×10^{21} ohm. cm.², whereas the summer minimum, at 2 h., is only 1.4×10^{21} ohm. cm.², almost the same as the resistance over the oceans. Here, again, we have a fourfold increase.

So far, we have been concerned with the variation of the effective resistance of an air column. This effective resistance is virtually defined by the equation

$$V = iR,$$

V being the voltage at the top of the column, and i the air-earth current, and it is important to notice that R is not the same as r , the integral of the specific resistance at all heights. This integral is defined by

$$r = \int_0^h \frac{dz}{\lambda_1 + \lambda_2},$$

in which λ_1 and λ_2 are the conductivities due to positive and negative ions respectively, and h is the height of the column. That R and r are not the same, is on account of the "electrode effect." Owing to the fact that negative ions cannot pass upwards from the ground itself, the current at the surface is conveyed only by positive ions. At a moderate distance from the ground there is an excess of positive charge, and in addition to the conduction current there is a diffusion current carrying positive electricity upwards. Above the region in which the "electrode effect" is appreciable the potential gradient is related to the conductivity by the equation

$$\frac{\partial V}{\partial z} = \frac{i}{\lambda_1 + \lambda_2},$$

whereas at the surface

$$\frac{\partial V}{\partial z} = \frac{i}{\lambda_1}.$$

To allow for the transition, which must be gradual, we may adopt the hypothesis that at any height the gradient is given with sufficient accuracy by the formula

$$\frac{\partial V}{\partial z} = \frac{i}{\lambda_1 + \lambda_2} + ic \exp(-z/a),$$

a being a constant and c the value of $\lambda_2/[\lambda_1(\lambda_1 + \lambda_2)]$ near the ground. This formula, which reduces to the two preceding ones if $z \rightarrow \infty$ and if $z \rightarrow 0$ respectively, does not imply that the λ 's are constant. By integrating the last equation, we find that

$$R = r + ac.$$

By adopting a simplified theory concerning the nature of the electrode effect, I calculated that the value of a would be of the order 30 metres. In this calculation,⁶ it was assumed that λ_1 and λ_2 were independent of height, and that the coefficient of eddy-diffusion was also constant. It is known, however, from experiments at Kew that at that station, at any rate in the middle of the day, the potential gradient is nearly the same at 10 metres and at the ground. If our method of approximation to the value of $\frac{\partial V}{\partial z}$ is valid, then a must be considerably greater than 30 metres. Let us suppose that $a = 100$ metres, then with the average

⁶ *Terr. Mag.*, 1932, 37, 355.

summer values of the conductivities c is about 0.7×10^{18} ohm. cm., and $ac = 0.7 \times 10^{20}$ ohm. cm. As R in the same season is about 2×10^{21} ohm. cm., r is then about 3 per cent. less than R .

In winter there is generally less diffusion by eddy motion, and it may be surmised that $a = 50$ metres. In this season the average value of c is about 2.5×10^{20} ohm. cm., so that, according to our surmise, $ac = 1.25 \times 10^{20}$ ohm. cm. With R at the average winter value, 4×10^{21} ohm. cm. r is again 3 per cent. less than R .

As to diurnal variation of ac , it is to be noticed that when the air is stable at night, a is likely to be small as well as c , so that the product ac is small then; in the morning c increases before there is much convection; later in the day, c decreases and convection increases; there is therefore not much to guide us in deciding at what hour ac is likely to have its maximum value. It may be that ac , like R , increases through the daylight hours. There is no reason to suppose that the difference between R and r is at any time much greater than the 3 per cent. which has been estimated as the average proportion, but it may well be that the difference can reach, say, 10 per cent. In that case, a considerable part of the regular diurnal change of R must be ascribed to the varying vertical extent of the electrode effect. In using the generalisation which has been put forward, that the resistance of the atmosphere increases throughout the hours when pollution is occurring, it must be borne in mind that the generalisation refers to the effective resistance R , and not to the true electrical resistance r . Whether r really behaves in the same way must be left undetermined.

This discussion is, it must be admitted, rather inconclusive. It may serve, however, to draw the attention of physicists to the difficulty of interpreting such simple observations as those of potential gradient. Systematic observations of what was then called electric tension were commenced at Kew Observatory in 1843. We are still a long way from fully understanding their significance.

Kew Observatory.

ON SULPHURIC ACID MIST.

BY A. DOOLEY AND C. F. GOODEVE.

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Sulphur trioxide vapour, when passed in an air stream through water, is not appreciably absorbed, but is converted into a mist which is stable to acids and alkalis. On the other hand, when the vapour is passed through 98 per cent. sulphuric acid, it is practically completely absorbed. A number of theories have been suggested to explain this behaviour; for example, Sackur¹ thought that the sulphur trioxide was converted into an insoluble form, S_2O_6 .² A more acceptable explanation was put forward by Walker, Lewis and McAdams,³ who state that:

¹ O. Sackur, *Z. Elektrochem.*, 1902, 8, 77.

² I. E. Adadurov and D. V. Gernet, *J. Chem. Ind. Russ.*, 1931, 8, No. 18, p. 12, hold somewhat similar ideas.

³ W. H. Walker, W. K. Lewis and W. H. McAdams, *Principles of Chemical Engineering*, 1923, p. 42.

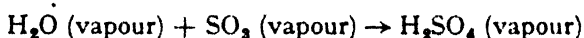
"If one attempts to dissolve the trioxide in water or dilute sulphuric acid, the trioxide vapour first comes in contact not with the liquid but with the water vapour which has evaporated from the liquid into the gas. It reacts with this vapour, producing minute droplets of sulphuric acid in the form of a fog, and these droplets are effectively insulated from the absorbing liquid by the gas film. One must therefore use as an absorbent (for the trioxide) ⁴ a liquid, the water vapour pressure of which is negligible, *i.e.*, strong sulphuric acid. This is the reason why for absorption one must use acid between 97 and 98 per cent. If more dilute, the pressure of water vapour is sufficient to produce a fog, if more concentrated the partial pressure of SO₃ over it is great enough to prevent complete absorption."

Recent experimental evidence strongly supports this latter explanation, and makes it possible to account more fully for the formation of sulphuric acid mist, and its various properties. In the first part of this paper, the whole mechanism is discussed, and in the second, the equilibria that obtain under various conditions have been calculated.

In problems dealing with sulphuric acid, it is very important to distinguish, as has been done by Miles,⁵ between the absorption of sulphur trioxide vapour and the removal of sulphuric acid mist. These problems are quite separate, and their solutions generally lie in different directions.

The Formation of Sulphuric Acid Mist.

Goodeve, Eastman and Dooley⁶ have recently studied the kinetics of the reaction between sulphur trioxide and water vapours. It was found that the primary reaction



was approximately stoichiometric and very fast. Under the conditions described (*i.e.*, at low pressures of reactants and a carrier gas pressure of about 5 mm.) about 1 collision in 100 between reacting gas molecules was found to be effective. This velocity corresponded approximately to the rate of termolecular collisions. It would probably, therefore, increase as the first power of the concentration of each of the reactants and of the pressure of the carrier gas. The fact that the reaction was not altered by careful purification of the gas to remove all particles of dust, led to the conclusion that the reaction was mainly homogeneous. These characteristics of the reaction resulted in a very narrow reaction zone, whose position was determined by the relative concentrations of the reactants and the diffusion velocities. The stoichiometric character of the reaction required that the rate of arrival of each of the reactants in the reaction zone should be the same, and, if the concentration or flow rate were altered, the zone would change its position until these conditions were fulfilled.*

The rate of arrival of water vapour at the reaction zone is a function of the concentration gradient which, in turn, depends on the rate of evaporation of water from a liquid surface. This latter problem has

⁴ The words in brackets are the authors.

⁵ F. D. Miles, *Manufacture of Sulphuric Acid (Contact Process)*, 1925, p. 209.

⁶ C. F. Goodeve, A. S. Eastman and A. Dooley, *Trans. Faraday Soc.*, 1934, 30, p. 1127.

* See Fig. 2, previous paper.

been studied recently by Alty and co-workers,⁷ who find that the rate of evaporation is approximately one-thirtieth of the rate of surface collisions for the saturated vapour. On the other hand, they find that the accommodation coefficient for transfer of energy of collisions of water molecules with a water surface, is unity. The accuracy of their experiments was not high, owing to necessary extrapolations, and it would appear that the value (α_0) for their first coefficient represents a minimum. The rate of evaporation of water into a vapour whose pressure is 1 mm. below the equilibrium pressure can, therefore, be calculated to be at least 2×10^{19} molecules per second per sq. cm. Unless the rate of arrival of sulphur trioxide is greater than this, the water surface will always be protected by a layer of water vapour.

This forms a starting point for the development of a three-stage mechanism of mist formation. The high velocity of the reaction producing molecular hydrogen sulphate does not permit the sulphur trioxide, as such, to reach the water surface. This hydrogen sulphate will be in a state of supersaturation and its concentration will increase until it reaches a critical value, whereupon condensation will occur with the production of agglomerates or nuclei of hydrogen sulphate. This is the second stage. The delay which occurs in reaching this critical point gives rise to the periodic phenomenon described in the previous paper. A few molecules of hydrogen sulphate will, however, penetrate the protecting water layer and enter the liquid water. The number that do this will depend chiefly on the distance between the reaction zone and the water surface.

The concept of the formation of nuclei of an involatile material as a necessary preliminary to the formation of a mist has been advanced by Townsend,⁸ and supported by Rothmund⁹ with regard to mists of sulphuric acid and iodic acid, and by Philip and co-workers^{10, 11} with respect to mists of hydrogen chloride.

The average number of molecules in these nuclei depends upon a number of conditions as yet not fully understood. This number may depend on the rate of condensation as normally controlled by the partial pressures, the number of foreign nuclei such as dust or ions, the rate of cooling of the carrier gas,¹² etc. Some important factors affecting its value are discussed by Freundlich.¹³ In addition, a theory based on initial aggregation of molecules has been proposed by Volmer.¹⁴ A theory of this type is favoured here, as it gives a simpler explanation of the delay in precipitation found in the periodic phenomenon. The size of the nuclei is of major importance in determining the equilibrium conditions of the mist, as will be discussed below.

The third and final stage in the process occurs when the agglomerates of hydrogen sulphate are carried by the air stream into a part containing excess of one or other of the reactants. This is absorbed until equilibrium is attained, resulting in the production of particles of strong light-scattering power which form the well-known sulphuric acid mist.

⁷ T. Alty and F. H. Nicoll, *Canad. J. Res.*, 1931, 4, 547; T. Alty and C. A. Mackay, *Proc. Roy. Soc.*, 1935, 149A, 104.

⁸ J. S. Townsend, *Proc. Camb. Phil. Soc.*, 1900, 10, 52.

⁹ V. Rothmund, *Z. Elektrochemie*, 1917, 23, 170.

¹⁰ R. W. Aldis and J. C. Philip, *J.C.S.*, 1930, p. 1103.

¹¹ C. N. Jackson and J. C. Philip, *J.C.S.*, 1934, p. 341.

¹² See B.P. 429 267 to Metallges, A. G.

¹³ H. Freundlich, *Colloid and Capillary Chemistry*, 1926, p. 769.

¹⁴ M. Volmer, *Z. Elektrochem.*, 1929, 35, 555.

The two types of mist described by Remy,¹⁵ and called "wet" and "dry" mists, correspond to the cases where the hydrogen sulphate nuclei pass into an atmosphere containing excess water vapour and excess sulphur trioxide, respectively. "Wet" mist consists, therefore, of droplets of sulphuric acid in various stages of dilution, and the "dry" mist, of droplets of oleum. Although these two mists are different as regards composition and some properties, their modes of formation are strictly analogous. For example, the periodic phenomena could be produced in an identical manner simply by reversing the relative concentrations of reactants.

The above mechanism has been demonstrated by a simple experiment in which air-sulphur trioxide mixtures were passed into a tube in which was placed a drop of water, as shown in Fig. 1. The clear space between the reaction zone and the liquid water was readily visible, as was also the carrying

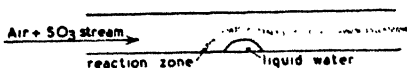


Fig. 1.

away in a thin layer of the sulphuric acid mist from the water. The drop was found to evaporate rapidly. Generally, however, the drop did not evaporate completely as some sulphuric acid diffused through to the water, was dissolved and lowered the vapour pressure of the water. This lowering resulted in an approach of the reaction zone and a still greater penetration of the sulphuric acid. Eventually, the whole system ceased to produce mists in the tube.

As was to be expected, the same phenomenon could be demonstrated by having water vapour in the air stream and a drop of strong oleum (about 50 per cent. free SO₃) in the tube.

The efficiency of removal of *sulphur trioxide* from an air stream is, according to the above mechanism, almost entirely dependent on the lowness of the vapour pressure with respect to SO₃ or H₂O. The importance of low partial vapour pressures of the absorbing medium has often been emphasised. Miles¹⁶ has shown by a series of experiments that the efficiency of absorption increases very rapidly with decrease of temperature. In the design of commercial plant, special precautions are taken, as described by Fairlie,¹⁷ to ensure that the final absorption is done with cold acid.

Presumably a solution of any non-volatile substance which will reduce the vapour pressure of water to a very low value could be used as an absorbing medium—that is, the power of absorption may not be specific to sulphuric acid.

The Stability of Sulphuric Acid Mist.

The stability of mists to alkalis, etc., has at times been attributed to adsorbed air films, electrical charges, etc.¹⁸ The existence of strongly adsorbed air films at liquid surfaces has not been proved, and is not to be expected, the low solubility of air in liquids indicating a low attraction between air molecules and liquids. Air cushions between colliding droplets of reasonable size are well known, but their effect in preventing contact on collision decreases very rapidly with decrease in droplet size.

¹⁵ H. Remy, *Z. Elektrochem.*, 1922, **28**, 467.

¹⁶ F. D. Miles, *loc. cit.*, p. 250.

¹⁷ A. M. Fairlie, *Sulphuric Acid Manufacture*, 1936.

¹⁸ See W. E. Gibbs, *Clouds and Smokes*, 1924, p. 96.

A thermodynamic metastability of aerosols due to adsorbed electric charges of one sign, as occurs with ordinary liquid colloids, is not possible in a medium of very low dielectric constant. In addition, Remy and Koch¹⁹ found that mist particles of sulphuric acid were uncharged.

The whole subject of the stability of aerosols has been made clear by the work of Tuovila and of Whytlaw-Gray and collaborators.²⁰ It has been found for stearic acid that every collision between mist particles results in their coalescence, and that the so-called stability can be entirely accounted for by the low diffusion velocity and low collision frequency of the particles. This indicates that adsorbed air films and electric charges, if present, were without effect.

Although no quantitative experiments have been performed for sulphuric acid mist, there is no reason to doubt that the same conditions apply, and therefore we can assume that the "resistance" of sulphuric acid mist to scrubbing agents is simply an indication of the low diffusion velocity.

Equilibrium Conditions for Sulphuric Acid Mist.

Although the stability of mists with time is only an apparent one, the particles themselves come into true thermodynamic equilibrium with the reactant vapour which happens to be in excess. The case in which water vapour is in excess is considered in the following. It is possible to obtain an equilibrium even when the partial pressure of water is equal to that over a pure water surface. Townsend⁸ derived an expression for the radius of a droplet in a water-saturated atmosphere, in terms of the osmotic pressure "of the soluble body." He equated the increase in vapour pressure due to curvature, as given by the Kelvin equation, to the lowering of vapour pressure of water corresponding to the osmotic pressure. Rothmund⁹ obtained a similar expression,²¹ using Raoult's law and the Van t'Hoff factor i . For an iodic acid mist, he found agreement between values for the radius so obtained, and as calculated from the rate of fall using the Stokes-Cunningham relationship. These equations can only be used for large particles where the approximations are valid, and for droplets in equilibrium with saturated water vapour. Under conditions other than these, as is shown below, the equilibrium radius is practically independent of concentration, except for droplets containing a given number of sulphuric acid molecules.

In order to follow the increase or decrease of size of a mist particle resulting from a change in the vapour pressure, it is necessary to proceed in another way. For a given droplet, the one important quantity which does not vary is the content of hydrogen sulphate, *i.e.*, the size of the initial nucleus. This may, however, vary considerably for droplets formed under various conditions. The variables concerned are inter-dependent, and this inter-dependence is not of a simple form. It is not useful to attempt a single equation to express the conditions obtaining in sulphuric acid mist. It is, however, possible to construct a series of curves showing the growth of droplets of sulphuric acid mist derived from

¹⁹ H. Remy and C. Koch, *Z. anorg. Chem.*, 1924, 139, 69.

²⁰ This question has been fully discussed in *Smoke* (1932), by Whytlaw-Gray and Patterson.

²¹ Care should be observed in using Rothmund's equations, as he has omitted the density in two of them. His last equation is correct as the density would have cancelled out.

hydrogen sulphate nuclei of various sizes in the presence of water vapour at various pressures.

The Kelvin equation for variation of vapour pressure with curvature is derived thermodynamically²² in, for example, Guggenheim's *Modern Thermodynamics*.²³ This equation may be written—

$$RT \log_e \frac{P}{P_0} = \frac{2\gamma}{r} \frac{dv}{dn} \quad (1)$$

where R is the gas constant, T the absolute temperature, P and P_0 the vapour pressures over the droplet and corresponding plane surface respectively for the same strength of solution, γ the surface tension, $\frac{dv}{dn}$ the partial molar volume and r the radius. The quantities P_0 , γ and $\frac{dv}{dn}$ are all functions of concentration, and these functions can only be expressed in the form of experimentally determined curves. These have been drawn in Fig. 2, the temperature throughout being 20° C. The

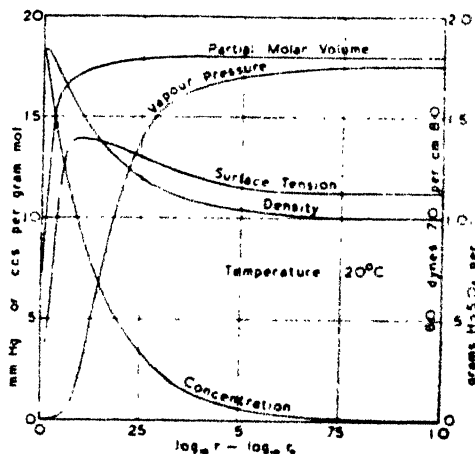


Fig 2 Physical Properties of Sulphuric Acid as used in equation 1

values of P_0 were taken from the International Critical Tables,²⁴ of γ from the results of Linebarger²⁵ (corrected for the now accepted value for water), and of $\frac{dv}{dn}$ from

the specific volume-concentration curve by the method of intercepts.²⁶ In obtaining Fig. 2, the values of the concentration in grams H_2SO_4 per c.c., were first plotted against $\log_{10} \frac{r}{r_0}$ (where r_0 is the radius of the initial nucleus of hydrogen sulphate), a purely geometrical calculation. Values of the

other variables were then plotted through this concentration on the $\log_{10} \frac{r_0}{r}$ scale. All of the essential data are shown in this figure.

The quantities γ and $\frac{dv}{dn}$ are also functions of the radius. The amount of the correction for change of surface tension with curvature has apparently not been calculated, but would be of minor importance at diameters above 10^{-6} cm.—that is, where the curvature is small compared with that of the molecules. The correction for variation of partial

²² A number of kinetic derivations have also been made. For example, see S. W. Gorbatschew, *Kolloid Z.*, 1935, 73, 263.

²³ E. A. Guggenheim, *Modern Thermodynamics*, 1933, p. 170.

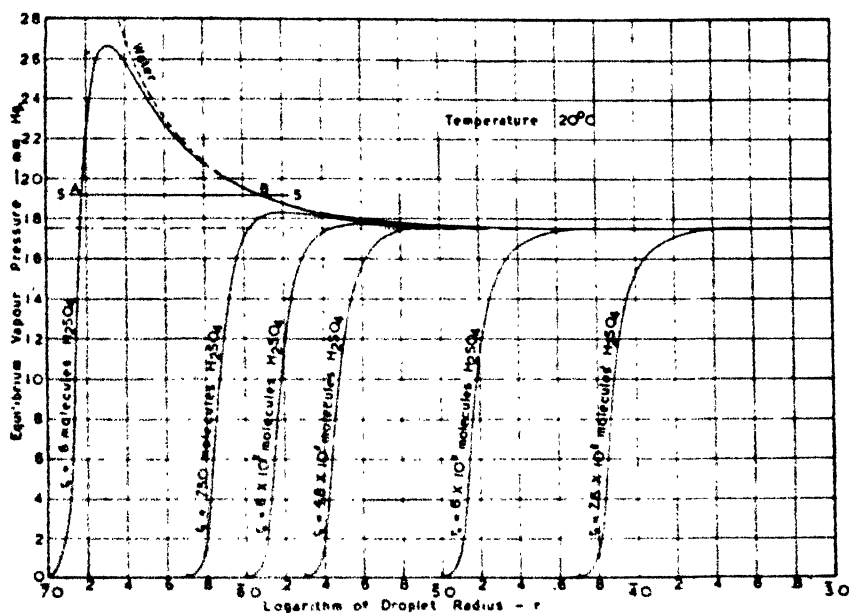
²⁴ Vol. III., p. 302.

²⁵ C. E. Linebarger, *J.A.C.S.*, 1900, 22, 5.

²⁶ Lewis and Randall, *Thermodynamics*, p. 38.

molar volume with curvature²⁷ is also very small, and most likely much less important than the change of surface tension. These corrections will be neglected here as we are generally dealing with droplets of sufficient size to give a strong Tyndall beam—*i.e.*, greater than 10^{-6} cm. The effect of electrical charges is also not considered.²⁸

Values for the equilibrium pressure P , over droplets of radius r , arising out of an initial nucleus of hydrogen sulphate of radius r_0 , have been calculated for a series of selected values of the latter, using Equation (1). The resultant members of a family of curves are shown in Fig. 3, the equilibrium vapour pressure being plotted against the logarithm of the droplet radius. The curves trace the history of the growth of the sulphuric acid droplets, excluding coagulation by collision, and show the equilibrium size to be expected when the droplets are carried in a gas containing water vapour at various partial pressures. When air carrying droplets of sulphuric acid mist is passed through liquid water, it becomes



appropriate point on the curve to the horizontal line, and will pass through a maximum as a large drop evaporates.

A similar set of curves may be plotted for the case of H_2SO_4 nuclei in an atmosphere containing gaseous SO_2 . The vapour pressure of SO_2 over the various strengths of oleum would then be represented by P_0 , and the other physical properties of this material would be used where required. These curves would be useful in considering the general properties of oleum mists.

A comparison of Fig. 3 with Fig. 2 will show that the variation of vapour pressure with concentration is the major factor in determining the equilibrium pressure of the drop. The concentration does not depend markedly upon radius for a given partial pressure, and a determination of concentration cannot readily be used to determine the size of the droplets. A heterogeneous mist containing particles whose sizes are spread over a wide range will give effectively the same value for concentration as a homogeneous mist, so long as none of the droplets are below 10^{-6} cms. A number of experiments in which the mist was carefully collected and analysed and the water partial pressure measured, were carried out, and were in conformity with these conclusions.

For all of the curves shown in the figure, there is a definite point of intersection with the saturated vapour pressure line, but the angle of intersection and the height of the maximum decrease very rapidly with increase in initial hydrogen sulphate content. This maximum has no special significance beyond showing the amount of super-saturation which it is necessary to obtain in a gas before the particles can grow indefinitely. A pressure line corresponding to a supersaturation below the maximum (such as the line SS, Fig. 3) will cut a curve in two positions; only one of these, A, however, represents a stable system. This is the one corresponding to the smaller radius. A droplet whose conditions correspond to the point of intersection, B, would have the same vapour pressure as the surroundings, but, if an infinitesimal amount of water is added to, or subtracted from the droplet, it will immediately become unstable, and will either increase to infinity or decrease to the radius of the point, A. The point B represents a type of false equilibrium, and droplets at this point are in an unusual position in so far as the addition of water *reduces* their water vapour pressure and *vice versa*.

A number of interesting conclusions concerning the removal of sulphuric acid mist can be drawn from these results. Mist particles can be removed either by reducing their size so that their Brownian movement becomes very high, or increasing their size so that they settle out by gravity or can be thrown out by centrifugal force. Sufficiently small particles cannot be obtained merely by drying if the initial nucleus is greater than about 5×10^{-7} cms. radius, and below this size the vapour pressure of the medium does not make a very great difference to the Brownian movement of the droplets. It is more usual to remove sulphuric acid mist by settling or by centrifugal means.²⁰ A first requirement in obtaining large particles is to start with large hydrogen sulphate nuclei; the degree of supersaturation required being smaller, the larger the nucleus. Subject to the considerations given in a following paragraph, the particles can then grow to infinite size with a very small degree of supersaturation.

The curves explain the results of Remy,¹⁸ who found that pure water

²⁰ See paper by one of the authors (C. F. G.), this volume, p. 1218.

absorbed *sulphuric acid mist* much better than did concentrated sulphuric acid. A casual examination leads one to the reverse conclusion, as the intensity of a mist is always increased by passing through water, whereas it is decreased on passing through sulphuric acid. This is due, of course, to a very large change of particle size.

The absorption of mist by water has been demonstrated in the course of this research in a simple way. A long horizontal tube was half filled with water, and a stream of air containing sulphur trioxide passed in one end. The growth of mist particles along the tube was readily visible, and at low flow rates they fell to the water surface completely before reaching the end of the tube. With 30 per cent. sulphuric acid, on the other hand, no such growth or falling of the particles was observed.

These experiments illustrate the contrast between the absorbing media most suited for the removal of sulphur trioxide and sulphuric acid mist, respectively. For the former, extremely low water vapour pressure is essential, whereas for the latter saturated or supersaturated water vapour pressure is more effective. The overall efficiency of a washing tower will pass through a minimum as the absorbent liquid is changed continuously from 98 per cent. H_2SO_4 to pure water.

It remains to consider how long it will take for equilibrium to be established when the conditions of the carrier gas are changed. The rate of evaporation and condensation of water vapour from pure water has been determined experimentally by Alty and co-workers,⁷ and it is probable that for sulphuric acid the rate will be the same when multiplied by the relative vapour pressures. Very approximate calculations from their results indicate that in one second after changing the conditions of the carrier gas, equilibrium within a few per cent. will be re-established. Probably the most serious cause of lag in the establishment of equilibrium will be the change of temperature of the droplets due to the condensation or evaporation of the vapour. A theoretical treatment of this has recently been made by Fuchs.³⁰ Townsend⁸ showed that iodic acid mists could be rendered invisible merely by a passage through concentrated sulphuric acid, but that, on replacement of the water by subsequent bubbling through the latter, the original intensity of visible mist was obtained. Such experiments have been repeated with sulphuric acid mist in the present work, and it was found that strong drying agents, such as phosphorus pentoxide and concentrated sulphuric acid, readily reduced the size of the particles until they became invisible, and on passing over water, the mist again grew to its original density. These experiments were carried out in a long tube and the rate of increase of the size of the particles could be easily seen. The experiments were purely qualitative, but sufficed to show that equilibrium was re-established in a few seconds.

Other Mists.

Any volatile anhydride which reacts extremely rapidly and practically irreversibly with water vapour, producing a non-volatile substance, will almost certainly be only partially absorbed when passed in an air stream through water. Acetic anhydride, chlorine heptoxide and nitrogen pentoxide are additional examples of substances which act in this way.

³⁰ N. Fuchs, *Physikal. Z. Sowjetunion*, 1934, 6, 224.

In all these cases it is likely that the mechanism is the same as that described for sulphur trioxide in the first part of this paper.

It would also be instructive to draw vapour pressure-radius curves for mists arising from the anhydrides mentioned in the preceding paragraph. These curves would be similar to those in Fig. 3. As far as is known, the mists behave in the same way. Mists formed by the hydrogen halides with water (generally in the presence of foreign nuclei) belong to a more complex but especially interesting group. In these cases, both vapours are present in the gas phase. If the partial pressure of one of these vapours is taken as constant, curves representing the change in partial pressure of the other with radius could be plotted for droplets arising out of non-volatile nuclei of various sizes. These would be somewhat similar to those in Fig. 3. In the absence of nuclei, the curves would not fall below the equilibrium pressures for flat surfaces, and therefore no mist particles could be obtained except at high supersaturations. This is in agreement with the results of Aldis and Philip.¹⁰ Askew²¹ found that mist formed more readily with hydrogen bromide than with the chloride. This follows from the much lower partial vapour pressure of the bromide over its aqueous solutions.²² It may be that the discrepancy between the calculated and observed sizes of hydrochloric acid mist droplets found by Jackson and Philip¹¹ would be removed if consideration were given to the above points.

Summary.

Recent measurements of the velocity of the reaction between sulphur trioxide and water vapours and the phenomena accompanying the production of sulphuric acid mist, are shown to support the explanation of Walker, Lewis and McAdams for the non-absorption of sulphur trioxide in water and its absorption in concentrated sulphuric acid. It is also shown that the size of the initial hydrogen sulphate nucleus is the important factor governing the change in droplet size with the change in the water vapour pressure of the medium. Curves have been drawn showing the growth of mist particles under various conditions, and their technical importance discussed. It is suggested that these considerations can be applied to other mists.

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²¹ H. O. Askew, *J.C.S.*, 1927, p. 906.

²² Measured by S. J. Bates and H. D. Kirschmann, *J.A.C.S.*, 1919, 41, 1991.

THE REMOVAL OF MIST BY CENTRIFUGAL METHODS.

By C. F. GOODEVE.

The problem of removing droplets of oil or other liquids from air has been recognised as a difficult one. Very small drops (radius less than 10^{-6} cms.) with high Brownian motion are easily removed with filters, as they collide readily with the walls. Large drops (radius greater than 10^{-4} cms.) have a negligible Brownian motion, but may be taken out

easily by centrifugal separation. The removal of droplets of sizes in the intermediate range has not been completely accomplished, except by electrostatic precipitation methods. In this paper, centrifugal methods developed in the course of work on mists of various types are described.

Impinging Gas Stream Methods.

The method for the detection and removal of mist droplets, in which the air stream is caused to impinge as a fine jet against a clean glass plate, has been applied by many experimenters with considerable success. The

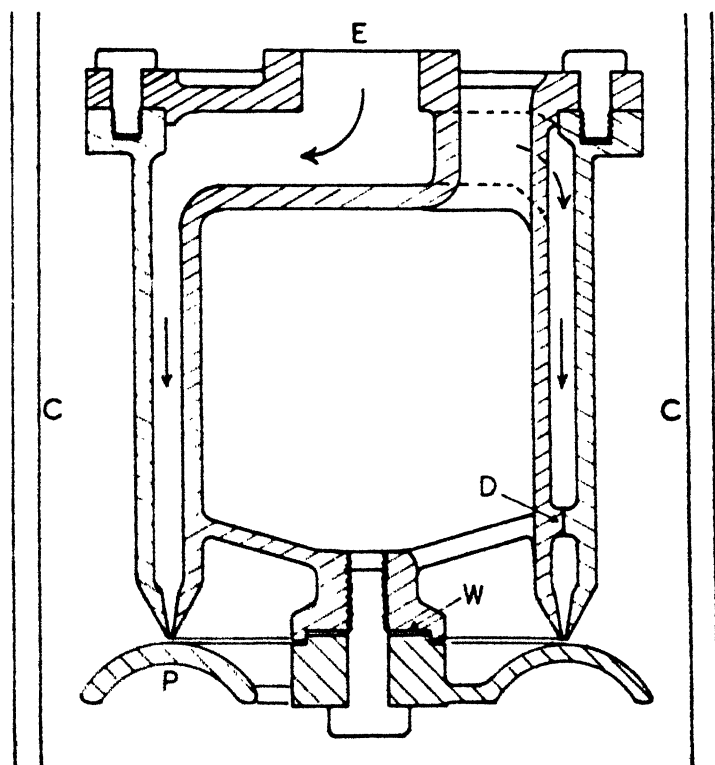


FIG. 1.—Cross-section of separator unit for the removal of mist droplets. E—Entry. D—Distance lugs. P—Collecting plate. W—Adjusting washers. C—Wall of container.

action depends on the centrifugal force on the particles during the rapid change in direction. This type of apparatus was modified by Calder and Fox¹ for use in the technical removal of sulphuric acid mist. In their original design, they used a large number of holes in plates arranged in series. They have improved their apparatus from time to time, and, in particular, they have found it more useful to apply a very high centrifugal force for a short period rather than a lesser force for a longer period.

The apparatus of Calder and Fox has the disadvantage that relatively wide jets have to be used to prevent stoppage and to give a reasonable capacity to the apparatus. These wide jets cause a reduced efficiency.

¹ Calder and Fox, *B.P.*, 1916, 126,320; 1922, 206,229; 1923, 228,646; 1924, 240,224.

In the apparatus described below, this difficulty has been avoided by using a narrow annular jet which allows a high capacity with a very short distance for the droplets to move transversely through the airstream. This apparatus has been used for some years on a technical scale to remove the mist droplets in the compressed air supplies (5 lbs. per sq. in.) of this laboratory and a number of others.

The final design of the apparatus, as prepared and made by Messrs. Reavell & Co., Ltd., Ipswich, is shown in the figure. The annular jet is $\frac{3}{4}$ in. wide and 12.4 ins. in circumference. Most of the pressure drop (generally 2 lbs. per sq. in.) takes place in the jet, producing a linear velocity of 370 ft. per sec. at the orifice. The air impinges against a collecting plate fitted close to the jet. The flow of the air is split into two parts, moving in opposite directions and at right-angles to the original flow, while the mist droplets carry on until they strike the collecting plate. The maximum thickness of air through which the droplets must pass is $\frac{1}{16}$ in. The air returns through the centre of the jet and along the outside, while the collected liquid falls through openings from the plate. The capacity of this separator unit for a 2 lb.-pressure drop is 30 cubic ft. free air per min. Generally two or three of these are used *in parallel* and are connected directly to the compressor.

Tests have been made on the content of oil droplets in the compressed air supply (arising from the high-speed rotary compressor) from time to time during the past three years. The separator units have been found to remove all oil droplets large enough to settle out and produce oil films in glassware and apparatuses commonly used with compressed air in the laboratory. Occasionally, however, it has been found possible to detect traces of oil by the jet and glass plate method referred to above. The units have not been found to remove completely the dust generally found in London's atmosphere. The efficiency may be increased by using a higher pressure drop and a smaller jet. The dimensions given, however, are convenient for general purposes.

The units have been examined every year and only a very small amount of grit has been found to collect in the annular jet. They have not been found so efficient for the removal of oil droplets in high-pressure air, owing, presumably, to the higher density of the medium through which the droplets must pass and to the greater turbulent motion produced at the jet. It may be possible to modify the design by the application of hydrodynamical principles to produce a device suitable for this purpose.

Filters.

The action of filters in removing mist droplets is mainly centrifugal¹—droplets much smaller than the sizes of the pores being readily removed. A very simple and efficient filter has been formed from a layer of glass or silica powder on coarse sand. The finest grade of Jena sintered glass filters, No. 4, has an equally high efficiency and is very convenient to use. The pore size of this filter has been estimated by the makers² to be 2 to 5×10^{-4} cm.

These filters have been tested with various mists. For example, sulphuric acid mist has been made under controlled conditions and tested before and after passing through the Jena filter, with a Tyndall beam from a Pointolite lamp. The size of the mist droplets was reduced continuously by lowering the partial pressure of the reactants until the blue mist just disappeared. It is estimated that the size of the droplets before the mist disappeared was 10^{-4} cms. In all cases no trace of a Tyndall beam could be seen in the air which had passed through the filter. Similar tests were made with hot exit flue gases from a power station boiler, with the same

¹ W. E. Gibbs, *Clouds and Smoke*, 1924, p. 88.

² See J. W. McBain and C. R. Dawson, *Proc. Roy. Soc.*, 1935, 148A, p. 32.

result. Some filters have, however, been found to pass a certain amount of dust from the atmosphere, as detected by the single jet described above. Particularly is this the case when the filters were new and dry, but their efficiency always increased when used.

Although no evidence has been obtained to show the removal of droplets whose size is below that necessary to give a Tyndall beam, it is unlikely that such droplets pass through the filter. Freundlich⁴ has shown that, with a coarser filter, the optimum transmission occurs for droplets of 10^{-4} cms., and that droplets below this size are readily trapped by their Brownian motion.

These filters have often been used for determining the amount of sulphuric acid present in London's atmosphere in the presence and absence of fog. A high velocity of flow was obtained by connecting the filter to the suction side of a vacuum pump, the discharge side being connected to a gas meter. They have also been used to measure sulphuric acid mist in exit flue gases. They have the important advantage of being inert to acids and they are readily cleaned. They may find uses in other problems connected with the analysis of mists.

It is important to recognise that filters do not give the concentration of the mist droplets but only the total content of the non-volatile components.

(Added in Proof.)

Removal of Fogs and Smoke by Falling Drops.

The interesting problem of the removal of smoke or fog particles by falling raindrops has been referred to by Dr. Dobson. A particle in the path of a falling drop will be caught, providing its inertia is sufficient to overcome the outward flow of air in front of the drop. It can readily be seen that the chance of a particle being so caught will be unity if it lies on the axis of the path, but will fall rapidly as its distance from the axis increases. The chance will also increase as the velocity of the falling drop is increased. The relation in this case is, however, rather complicated. Heavier particles will, of course, be trapped more easily than lighter ones.

A few experiments were made with an apparatus in which a drop of a definite size could be maintained on the end of a very fine capillary tube in an upward flowing air stream containing sulphuric acid mist. It was found possible to vary the size of the drop and the velocity of the air stream over quite wide limits. Measurable quantities of sulphuric acid were found in the drop after a short run but the effects of the variables referred to above were not studied.

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⁴ H. Freundlich, *Colloid and Capillary Chemistry*, 1926, p. 785.

GENERAL DISCUSSION.*

Dr. B. W. Bradford (*Billingham*) said: The curves given by the authors (Fig. 3) for the growth of sulphuric acid droplets refer rigidly only to aerosols at infinite dilution. In practice, aerosols of the concentrations usually encountered in any but meteorological work aggregate so rapidly that vapour-pressure equilibrium cannot be attained except in the final stages of growth, when the particle concentration has diminished to very low magnitudes.

* On the two preceding papers.

Particle size determinations by several methods on a highly concentrated sulphuric acid mist (15 g./M³) produced by hydration of SO₃ in the presence of excess water vapour, gave concordant results, which agreed well with the rate of aggregation calculated from the Einstein-Smoluchowski formula. A particular search was made for inhomogeneities of droplet radius: it was found, however, that the variations were less than the experimental error of about 5 per cent.

In the practical determination of mist concentrations in saturated gases by methods involving a sudden pressure drop (*e.g.* filtration or impingement) it is important to note that the apparent mist concentration may be appreciably increased by condensation of vapour due to cooling by expansion at the orifice. This source of error is usually greater than that due to the fact that vapour pressure equilibrium in the aerosol refers to a highly curved surface while in the mist-sampling apparatus the surface on which the scrubbed mist collects is approximately plane.

Professor H. Köhler (*Uppsala*) said: How does Dr. Goodeve explain the condensation in a Wilson chamber, where the supersaturation is so great. Again, does the Aitken Nucleus Counter really give the number of nuclei; it is generally believed that the number of droplets formed, is the same as the number of nuclei.

Mr. C. F. Goodeve (*London*) (*communicated*): Clusters will be stabilised if given an electric charge, owing to the increased attraction to the polar water vapour molecules. Nuclei will, in general, facilitate condensation and, if present in sufficient numbers, prevent the attainment of the degree of supersaturation necessary for the growth of clusters to droplets. Under most conditions, therefore, the Aitken Nucleus Counter will probably give the correct result.

Dr. N. Fuchs (*Moscow*) (*communicated*): To the three stages of formation of a sulphuric acid mist mentioned by Dooley and Goodeve, one more must be necessarily added, namely the coagulation of the growing nuclei and of the finally developed droplets. The rôle played by coagulation in the formation of the sulphuric acid mist can be seen, *e.g.*, from our experiments in which, by a quick mixing of two air-jets containing vapours of water and sulphur trioxide at partial pressures of about 1 mm., a primary mist was formed containing about 10¹¹ droplets per c.c. of 1.2 to 1.5 × 10⁻⁶ cm. radius. Such a mist coagulates with a tremendous velocity, and in one second the number of particles per c.c. is reduced about a hundredfold, and the mass of the droplets accordingly increased.

Mr. A. Dooley (*Birmingham*) (*communicated*): It is incorrect to say that the Calder-Fox Scrubber is limited to "wide jets used to prevent stoppage and to give a reasonable capacity to the apparatus." In a modified form, now in general use, the scrubber is built up of glass strips arranged to give narrow slits behind which are supported further strips on edge. This design permits the adoption of the most suitable dimensions and clearances for any particular purpose. Units with 1/32-inch slits are in use on, for example, sulphuric acid concentrators but, if necessary, 1/64-inch slits could be arranged by using ground glass strips.

Blocking of the slits by solid matter depends on slit dimensions, and on the position and arrangement of the striking or "back" plate. In the Calder-Fox apparatus referred to above, overlap of the "back" strips is a minimum. No advantage in this direction could be claimed for Mr. Goodeve's apparatus.

While admiring the design of Goodeve's apparatus in so far as it is applied to the particular purpose stated, *viz.*, the removal of oil mist from 30 cubic feet of air per minute, I feel it necessary to point out that there would be serious limitations to its application to systems on which the Calder-Fox Scrubber is employed. On a technical scale gas volumes of upwards of 1000 cubic feet per minute are frequently handled, and it is evident that a circular form of apparatus would be unwieldy if in one unit or, if the necessary capacity were obtained by multiplication of

smaller units, unnecessarily complex. Furthermore, the question of materials of construction would require consideration if corrosive fumes were to be handled, and here also the Calder-Fox Scrubber appears to have the advantage.

Dr. N. Fuchs (Moscow) (communicated) : The chief rôle in the removal of the droplets of 10^{-3} cm. radius and less by means of porous and fibrous filters is played, not by the centrifugal forces, but by the Brownian movement of the droplets. This may be seen, *e.g.*, from the fact that such droplets pass the filter more easily the larger the linear velocity of flow through the filter. Centrifugal forces would evidently give the opposite relationship. The same conclusion may be reached theoretically by calculating the effect due to inertial forces by the method of Albrecht.¹

It is difficult to estimate correctly the efficiency of the glass filters spoken of by Goodeve in respect to sulphuric acid mists, because he does not indicate the velocity of flow in his experiments. It is doubtful whether the finest mists in these experiments consisted of droplets as large as 10^{-4} cm. As was shown in our laboratory,² no Tyndall beam can yet be observed in highly concentrated (10^9 droplets per c.c.) sulphuric acid mists with droplets of even 3×10^{-4} cm. diameter (arc lamp illumination.)

Mr. C. F. Goodeve (London), said :

In reply to Dr. Bradford and Dr. Fuchs : The vapour of a droplet formed as a result of a collision between two droplets remains practically unchanged except when the droplets are below visible dimensions. This can be confirmed by a careful examination of Figs. 2 and 3. It is, of course, impossible to represent, in a single diagram, all variables which occur in practice.

In reply to Dr. Bradford : I have emphasised in my paper on centrifugal methods that it is impossible to determine a mist concentration (expressed either as number of droplets or grams, per unit volume) by any apparatus in which the droplets are removed. This arises from the fact that removal invariably alters the surface area and curvature. Centrifugal methods can only be used to determine the concentration of a non-volatile constituent of a mist and, of course, condensation of vapour due to cooling does not in any way enter.

In reply to Mr. Dooley : I agree that the modified form involving the use of glass strips is a considerable improvement over the previous type of apparatus. Unless wedge-shaped glass strips are used, however, there will be a very large loss of power in obtaining the linear high-speed flow desired for efficient removal.

¹ Albrecht, *Physikal. Z.*, 1931, **32**, 48

² Fuchs and Oshman, *Acta Physicochimica U. R. S. S.*, 1935, **3**, 61.

PART II. : THE INDUSTRIAL ASPECTS OF DISPERSE SYSTEMS IN AIR AND GASES. INTRODUCTORY PAPER.

BY R. LESSING.

Received 14th April, 1936.

Disperse systems in gases in their relation to the problems of industry and the amenities of life have not yet received the close study which their ubiquity and practical importance demand. The present survey is therefore not intended to be a record of work done, but to indicate the problems which still await solution and the directions in which the results

of fundamental investigations can and should be applied in practice. The dispersoids to be considered comprise solids, liquids, solids covered with liquid films and liquid droplets containing solid nuclei.

Some of these systems happen to occur in many industrial operations, some form natural phenomena of climatic conditions, others are undesired concomitants of the atmosphere peculiar to civilised conditions of life and work, whilst yet others such as war gases and smoke screens, are set up intentionally as products of the latest developments of human activity.

Dust.

The most common and quantitatively most important solid dispersoids are dusts. Systems containing these are probably also the simplest, and may therefore be considered first.

The most prolific source of dust production by man is grinding for size reduction, and this operation is carried out in the manufacture of flour, cement, fertilisers, coal, lime, chalk, gypsum, pigments, dyes, glass and pottery materials, rubber fillers, fish meal, potato meal and others. The total production of these materials in powder form approaches 20,000,000 tons per annum in this country.

All these industries comprise processes in which at some stage dust is dispersed in air. For reasons of economy, health and comfort, it is necessary to recover this dust and purify the air; hence, apparatus for dust collection is an essential component of their equipment.

Other types of dust, produced by abrasion, occur in the surface grinding, polishing and sandblasting industries. The quantities involved are of a much smaller order, but collection is not less difficult on account of the multiplicity of point sources of dust emission and their proximity to the respiratory organs of the workers.

Into this category falls the dust formation by drilling shot holes in mining and quarrying operations. In coal mining and handling, dust is raised in large quantities and high concentrations during blasting, loading and unloading, and particularly in screening. Some of this is formed by the disruptive action of explosives on the shale or sandstone and on the massive coal, and some is due to the dispersion of the more friable components of the coal seams. An intentional application of dust takes the form of "stone dusting" of underground roadways and working places for the prevention of coal dust explosions. There is at least one form of dust, *viz.*, road dust, that is rapidly diminishing, and has already disappeared from our principal highways, which are no longer constructed with waterbound, macadamised surfaces liable to severe attrition.

A problem affecting every individual is that of domestic dust and its collection after settlement by sweeping or by modern suction methods.

Smoke.

True smokes, defined as dispersions in gases of solids formed by condensation and aggregation or coagulation occur in practice mainly in metallurgical operations in which metals or metallic oxides are volatilized by heat, either in bulk as in the "distillation" of zinc, or as the result of unavoidable side-reactions, as in most smelting operations. The recovery of valuable metals dispersed in waste gases as smokes is an important adjunct of modern metallurgy.

Common domestic "smoke" cannot strictly be grouped among the true smokes for reasons discussed below; the only true type of carbon smoke is the system formed by complete thermal decomposition of hydrocarbons or other volatile carbon compounds in which no liquid products are left.

Fog.

Fogs are usually regarded as dispersions of liquids in gases, but it is questionable whether pure liquids are capable of fog formation without the aid of heterogeneous nuclei. Neither in meteorology nor in industry can systems be contemplated which are free from solid particles or substances soluble in the liquid dispersoid. Any definition of fogs as the formation by condensation of liquid droplets in the gas phase, must therefore comprise the presence or formation of dust or smoke particles, or of compounds soluble in the liquid phase. In practice, matters are complicated by the presence of a number of different kinds of particles or compounds, some of which are frequently unidentified and of unknown structure, composition and effect. The meteorological aspects of fog formation do not come within the scope of this paper, except as far as the supply of solid nuclei and of sulphur oxides from flue gas emission is concerned. The bulk of the chloride nuclei are, of course, derived from sea-water spray, but some hydrogen chloride is due to chloride in coal released upon its combustion.

An industrial fog of considerable technical importance is the tar fog in crude coal gas and coke oven gas. The tar droplets formed in the gas leaving the carbonising retorts or ovens by the rapid drop in temperature, give it the typical reddish-brown colour. I am not aware of any precise work on the structure of the droplets, their size distribution, and rate of coalescence, but there cannot be any doubt that the "free carbon" particles formed by the thermal decomposition of the primary decomposition products of coal, are the nuclei on which the liquid tar, together with water, or rather a solution of ammonium salts, condenses. The "free carbon" still contains several groups of asphaltic or bituminous substances.

The dispersoids of tar fog are therefore themselves a multiphase system; the principal phase is a complex mixture of hydrocarbons, oxygenated bodies, bases and pitch, and has a wide boiling range. They are dispersed in a gas phase containing, *inter alia*, the lower boiling hydrocarbons, which are solvents for the condensate. This system, which rapidly passes through a temperature gradient from 900° C. to 15° C., offers an interesting field of investigation. The persistence of some residual tar fog through the condensing system and the following gas purifying train, has recently led to the installation of electrical tar precipitators for the almost quantitative extraction of tar in fog form.

The formation of "gum" in coal gas is a phenomenon which has only recently become apparent since the adoption of the practice of eliminating naphthalene and some of the benzene hydrocarbons from the gas. The cause of "gumming" is not yet fully explained, but it is probably due to the action of nitrogen oxides on certain gas constituents; the reaction products are peculiar in coalescing from the dispersed state to tough masses when the gas passes through narrow orifices or channels.

In the manufacture of sulphuric acid, and particularly of oleum, the waste gases carry droplets of the acid in fog form. Presumably there are sufficient fine dust particles present, some of which are lifted from the

catalyst or catalyst carrier, which act as nuclei for the drop formation. This industry and the sulphide roasting industry were among the first to employ electrical precipitation for breaking up these very persistent acid fogs.

Oil fogs occur widely ; the most common form is that of the exhaust from motor engines, where solid nuclei are always provided by the " carbon " formed on incomplete combustion of the petrol air mixture. The oil fog from the lubricants of gas compressors is probably formed by a different mechanism. Decomposition at high temperatures does not take place and the cause must be sought in the stripping of the oil film on the cylinders at critical gas velocities.

The persistent fogs resulting from fatty acid distillation, rosin distillation or gum running must be classed as smokes, inasmuch as the dispersoids in the cooled system are more or less solid.

The Flue Gas Problem.

The burning of fuels results in the creation of disperse systems in gases whose practical importance is only equalled by their theoretical interest and technical complexity. Even in the case of the combustion of gases—complicated enough *per se*, but relatively simple in comparison with that of solid fuels—disperse systems may be set up in the absence of a suitable excess of, or inadequate mixing with air, resulting in a smoky flame.

Liquid fuels in drop form are dispersed in air by spraying into the combustion chambers of furnaces or into the cylinders of internal combustion engines. The velocity and completeness of combustion depend, apart from the chemical and physical characteristics of the fuel itself, upon the subdivision and disposition of the liquid in the gaseous phase. The mechanism of " knock " during combustion under high compression has been studied intensively during recent years and the various theories advanced for it depend on the correct interpretation of the structure and behaviour of the disperse systems involved.

The combustion of coal provides a vast field for the study of disperse systems in gases. Quantitatively, its importance may be gauged from the fact that the portion of coal emitted from industrial and domestic chimneys constitutes the great bulk of the polluting matter dispersed in the atmosphere of civilised countries. For a thorough understanding of the kind and amount of this emission it is necessary to consider the chemical and physical characteristics of the fuel itself, its behaviour during the combustion process and the products resulting from it.

Coal is in every respect a most heterogeneous material, as is obvious from the great variety of vegetable matter which has formed the raw material, the manner of its deposition and the different biological, chemical and geophysical agencies which combined to transform this material into coal as we find it. The different kinds of coal characterised by containing four distinct rock types (vitrain, clarain, durain, fusain) in different stages of " coalification " (rank) determine the behaviour of the fuel during the combustion processes. With each of these are associated inorganic substances of characteristic composition and in characteristic proportions, together with adventitious mineral impurities derived from the strata below, above and between the coal seams.

The mechanism of combustion in a fuel bed is complicated by the fact that combination with the oxygen in the air can only take place on the

surface of a piece of coal. The rise in temperature causes layers below the surface to be subjected to thermal decomposition (carbonisation) by which combustible gas and tar are liberated. Under the aerodynamic conditions controlling the burning mechanism, some of this volatile matter escapes so rapidly from the high temperature zone that its combustion is not completed. Unless it is subjected to contact with hot surfaces such as a furnace arch, and possibly to the action of secondary air, a portion will escape in form of tar suspended in the flue gases. Some may be heated high enough to suffer secondary thermal decomposition, but only after a time lag long enough to permit its escape from the combustion zone. In this case "soot" is formed. Firing conditions permitting the escape of tar vapour or soot do not obtain in modern, well-conducted furnace operations. They are, however, the concomitant of the customary management—or lack of it—of the open fire in the domestic hearth. The tar content of deposits from the atmosphere of towns can therefore be traced back with certainty to this source and its amount forms a measure of the chimney emission from domestic fireplaces in which raw coal is burned.

The portion of the organic coal substance which is emitted from industrial furnaces or any fires operated with air and flue gas currents of high velocity, is in form of coke particles or partially burned coal particles. The former are frequently cenospheres formed by the swelling and blowing into bubbles of individual coal particles during a carbonising stage which was arrested when the empty shell was completely coked and had assumed rigidity, the hollow particle escaping from the furnace and combustion by reason of its balloon-like structure and low volume-weight. Coke cenospheres are formed in great number in pulverised fuel fired furnaces, where the sub-division of the raw coal into fine dust particles favours the occurrence of this phenomenon.

Relative to its proportion in the coal fired, the ash contributes a much greater quota of polluting matter than the combustible coal substance. The reasons for this are closely bound up with the character of the various mineral substances in the coal components and their behaviour during combustion.

The position is fairly simple in the case of burning coal in powder form. Here small coal particles, irrespective of the components they represent, are individually subjected to combustion dispersed in about 13,000 times their own volume of air, so that they are rapidly and fairly completely burned. Each particle of coal leaves its ash, again in particulate form, suspended in the flue gas. Owing to differences in their composition, these ash particles behave in different manner. Those of low fusion point are at the furnace temperature in form of liquid drops. Some of these drops, mostly in form of hollow spheres or ovoids, pass forward and retain these shapes when cooled. Many collide with each other and coalesce—as in other liquid-gas systems—or attach themselves to more refractory and still solid particles. When such aggregates become too heavy they are deposited at points determined by the velocity and the viscosity of the gases. Such sedimentation may cause the formation of masses of clinker (bird's nests). I have shown¹ that the size and basicity of ash particles or aggregates in a coal dust firing system diminishes from the combustion chamber towards the chimney, and that the solids emitted from the chimney may consist of highly silicious and refractory single particles.

¹ Lessing, *Trans. Second World Power Conference*, Berlin, 1930; *Fuel in Science and Practice*, 1930, 9, 348.

Pulverised fuel furnaces send forward about 70 per cent. of the ash in the coal fired, and dust extraction plants are therefore incorporated in most modern installations.

Coal fired in pulverised form accounts only for about 4,500,000 tons or 2.8 per cent. of this country's total consumption. The great bulk is fired in the size ranges obtained from the collieries, *i.e.*, pieces from 12 inches down to the dust particles naturally contained in coal. Some 90 per cent. of the ash remains behind, but the balance derived from coal particles detached by decrepitation or from minerals finely disseminated through the mass, is small enough in particle size to be carried by the current of combustion gases before coalescence with larger pieces can take place, and unless deposited in the flues, is emitted from the chimney.

It is worthy of note that the natural dust in coal, in which the charcoal-like fusain is concentrated, is particularly liable to be raised by the gas currents, owing to its non-caking character and consequent failure to fuse and coalesce during the carbonising stage. Much of this is therefore carried out of the fuel bed before the combustion is completed. Coal as mined contains about 4 per cent. of dust smaller than 350μ . The British consumption of 161,500,000 tons (1934) per annum included, therefore, 6,400,000 tons of this potential contribution to atmospheric pollution.

It is interesting to compare this with the total amount of solid matter found in the atmosphere, and the case of London may serve as an example. The coal consumed in Greater London in 1934 was 19,282,000 tons. Its mean dust content at 4 per cent. amounted to 771,280 tons, with an ash content of, say, 15 per cent. It may be fairly assumed that from this coal dust all its 15 per cent. ash and 7.5 per cent. of carbonaceous matter which has escaped combustion, are discharged into the atmosphere. This means a total of 173,500 tons of flue dust derived from coal dust and emitted over the 700 square miles of the London area. According to the 21st Report of the Atmospheric Pollution Committee the total deposit over these 700 square miles during the corresponding period (taking the mean of the amounts collected in all deposit gauges as representative for this area) was 184,000 tons. The portion of this total consisting of carbonaceous matter and insoluble ash plus one-half of the soluble ash (sulphates) amounts to 124,500 tons, and may be compared with the emission derived from the natural dust in coal. Whilst the pollution caused by coal dust appears to be actually greater, it must be remembered that perhaps only 15 per cent. of the solids suspended in the atmosphere settle or are washed out by rain and are caught in the gauges. Allowing for this, it appears that the natural dust in coal may be responsible for 20 per cent. of the pollution of the atmosphere with solids. As means for separating this dust are available, its elimination and utilisation under conditions permitting the collection of its ash would greatly assist in the abatement of the pollution of the atmosphere with solids.

The sulphur in coal, present partly in inorganic form in pyrites and partly in organic combination, is almost completely liberated during combustion. The greater portion escapes as SO_2 , and a small portion as SO_3 . I have given an estimate of the minimum annual sulphur emission over London² of 500,000 tons, expressed as sulphuric acid. Much of this remains in gas form, and a large part is retained by way of corrosion of metals, disintegration of building materials and action on textiles and

² *Nat. Smoke Abatement Soc., Proc. 7th Annual Conf., Bristol, 1935.*

other organic matter. From the point of view of disperse systems in gases, two forms must be considered; sulphuric acid nuclei present in town air, especially during fogs, and sulphate particles formed by the neutralisation of basic dust, notably lime, and oxidation during a stage of favourable p_H condition.

The presence of oxides of nitrogen (NO and NO_2) as normal constituents of combustion gas has not received much attention in the past, but is now becoming important in connection with flue gas washing processes. Their concentration in industrial flue gases is of the order of 0.1 to 0.2 mg. per litre in terms of nitrogen, but may vary with the combustion conditions. Apart from their probable effect on the oxidation of SO_2 , they are of interest in view of Coste and Wright's³ work on the formation of nitrous acid nuclei.

Chlorine, which is present in many coals in amounts up to 0.5 per cent., appears in the products of combustion mainly as alkali or iron chloride, or as hydrochloric acid, and thus adds a little to the chloride content of the atmosphere derived from sea-water.

The form in which fluorine, the presence of which in some coals has been established,⁴ is liberated on combustion is not yet known. In carbonisation it is present in the gas as hydrogen or ammonium fluoride. Though small in amount, this element will have to be regarded in future as a potential contributor to atmospheric pollution.

In the carbonising process accompanying or preceding combustion as in the domestic fire, indicated by liberation of tarry matter, ammonia is emitted which combines with SO_2 or SO_3 and causes the formation of water soluble nuclei. These (where dispersed in air) behave similarly to the nuclei of NaCl derived from sea-water spray.

Dust in Mining.

Coal causes dispersion of solids in the air even before it is burned. In mining, dust is released and is carried by the currents of ventilating air and precipitated from them in the workings. The risk of its inflammation and of underground explosions caused by it is an important subject of investigation by those concerned with the safety in mines. The physical and chemical mechanism of the use of stone dust to prevent explosions requires still to be fully explained.

In the preparation of coal on the surface, the effective collection of dust from the air, notably in screening operations, is as yet an unsolved problem.

The silicious rocks associated with coal are responsible in some districts for a considerable number of cases of silicosis. The problem of the prevention of this terrible disease calls for the close study of suspension in air of particles of quartz, shale, sericite and other minerals, of sizes below 5μ formed by drilling, shot firing and other underground work. In some operations as in drilling, dispersions of the coarser dust may be avoided by suitable filters. For the fine dust raised by shot-firing, spraying with water and wetting agents is being experimented upon. Fundamental work has only recently been undertaken, and it is hoped that the results of this symposium will be of use in the practical solution of this problem.

³ Coste and Wright, *Phil. Mag.*, 1935, 7, 20, 209.

⁴ Lessing, *Nature*, 1934, 134, 699; *Fuel in Science and Practice*, 1934, 12, 347.

A better knowledge of the principles of dispersion of solids in gas will also assist on the clinical side of silicosis, for the passage of the silicious matter through the respiratory system and its retention by the lungs involve phenomena not unlike those underlying the operation of industrial filters or scrubbers.

Methods of Cleaning Gases.

Industrial and meteorological disperse systems of solids or liquids in gases are, without exception, undesirable. The practical problems involved deal, therefore, with their breaking-up and the removal of the dispersoids from the gas phase. The methods principally employed are sedimentation in large chambers, centrifugal separation, filtration, electrical precipitation and washing with liquids in spray or film scrubbers.

Sedimentation involves the slowing down of the currents of gas carrying dust by expansion in chambers large enough in cross-section to permit the particles to settle out by gravity. Within the limits of space available in practice only the coarser particles settle effectively, although they may carry down some of the finer with which they collide in their downward path. In some cases baffles are provided to arrest particles by impact and turbulence is reduced by sub-dividing the current by means of vanes.

A common form of mechanical dust separator is the "cyclone," a cylindrical vessel into which the gas is introduced tangentially. The dust particles or droplets of liquid are thrown out by centrifugal force, arrested by friction on the wall of the cylinder and drop into the conical collecting base, whilst the gas leaves by a central tube. The efficiency for removing dust larger than 20μ may be fairly high if the apparatus is designed to keep particles once thrown to the periphery out of the turbulent zone near the vertical axis of the apparatus. Many special contrivances have been proposed to achieve this object, but the extraction of particles below 20μ requires a more intensive study of the size range and shape of each kind of dust, the temperature and viscosity of the carrying gas and a thorough exploration of the zones of streamline and turbulent flow in the vessel at varying gas velocities and pressure drops.

Filtration through fabrics or other porous layers provides a positive means of dust removal from gases. The disadvantage is the high resistance and its rise caused by the increase in the thickness of dust layers on the surface of the textile or other filter. Mechanical devices for shaking filter bags intermittently are usually employed. The permeability for fine particles varies with the original texture of the fabric, its age and condition and the thickness of the layer covering it. The need for sub-division into small units to avoid excessive resistance, makes the system very cumbersome where large volumes of gases are concerned.

In the thirty years since Sir Oliver Lodge's early experiments were applied in practice by Cottrell, electrical precipitation has been put to industrial use on an extensive scale. In broad outline the system is extremely simple. The gas to be purified is ionised by the corona discharge from negative electrodes of small radius of curvature (wires, thin rods, chains, grids); on their way to the positive, collecting electrode of large radius of curvature (tubes or plates) some of the ions attach themselves to the dispersoids, charge them and cause them to travel in the same direction. The electric current employed is of the order of 0.10 to 1.0 amps. at a pressure between 20 and 75 kv., the collecting electrode

being usually earthed. The technical development has been mainly concerned with means for producing, conducting and insulating against, the high-tension current required; with the form of the electrodes, the dimensioning of the gas passages and the design of rapping or other devices for removing dust from the positive electrode. In some cases the discharge electrode also collects some dust carried there by a minority of positively charged ions.

Much of the work done has been of an empirical kind, and was directed to the special needs of various branches of industry and the particular nature of the dusts, fogs or mists to be treated. The removal of liquids, say sulphuric acid or tar, from the collecting surfaces is easy, but dusts differ greatly in adhesiveness and conductivity and some may, by building up on the surfaces of the electrodes, affect the electrical conditions appreciably, so that non-conducting dusts may require moistening or the addition of conducting dust to the gas as well as mechanical vibration or scraping to keep the deposited layers of reasonable thickness and permeable to discharge.

The electrical precipitation industry has arrived at a stage of development where information on the properties of dispersoids, such as size, size distribution, shape, density, composition of particles, their surface properties and electrical conductivity, and the critical examination of the results will be of great assistance in its further development.

Washing of gases with water is probably the most effective method for the elimination of dispersoids in them. In gas works the scrubber packed with coke or wooden grids has served from the beginning of the industry for the extraction of ammonia and incidentally removes tar nuclei. Its modern equivalents are the rotary scrubber and towers filled with contact rings.

In air conditioning plants the control of humidity by water spraying devices is accompanied by the extraction of suspended solid particles. These plants usually incorporate eliminator baffles on which the un-vaporised excess of water in drop form is arrested.

The treatment of flue gases by wet methods has assumed considerable importance during the last few years. After the claims of the aggrieved owner of land damaged by sulphur gases from the Barton Electricity Works of the Manchester Corporation were sustained by a judgment of the House of Lords in 1929, the Electricity Commissioners insisted that at the new London power stations to be erected at Battersea and Fulham, the necessary steps should be taken to eliminate practically all the sulphur oxides from the combustion gases of their boilers before discharge to the atmosphere. The magnitude of the problem will be realised if it is considered that each of these power stations when completed and working under full load will discharge nearly 2,000,000 cubic feet of flue gases per minute, and that before washing they contain 1 grain of sulphur per cubic foot (2.3 mg. per litre) and 1.25 grains dust per cubic foot (2.8 mg. per litre).

In the preliminary work it was soon found that any method capable of extracting nearly all the sulphur will, *ipso facto*, remove the dust to at least the same degree, since dust is removed from the gas phase immediately it is wetted, whilst the absorption by water of SO_2 and its oxidation to SO_3 if desired, require a measurable time of contact.

The methods employed at Battersea and Fulham differ in several important respects. At Battersea⁵ a spray system is employed common

⁵ Hewson, Pearce, Pollitt and Rees, *Proc. Chem. Eng. Group*, 1933, 15, 67.

to all the boilers, the washing water is allowed to become acid in the first stage during which iron is added for the catalytic oxidation of SO_2 to SO_3 , and the effluent after neutralisation with chalk and clarification is discharged into the Thames. At Fulham an individual washer of the grid type is provided for each boiler, a lime or chalk suspension is continuously circulated in film form over the grids and only a small purge corresponding to the sulphur and dust extracted is withdrawn, clarified and returned into the cycle. The mud containing calcium sulphite, calcium sulphate and dust is discarded, but no effluent is sent into the river. In an auxiliary scrubber through which air is passed, the sulphite in the circulating liquor can be completely oxidised to sulphate, if required.

In the experimental work carried out in connection with the Fulham plant, I found that the principal difficulty did not lie in achieving the high sulphur extracting efficiency stipulated, but in preventing the incrustations of calcium sulphate deposited on the scrubbing elements. These were traced to excessive supersaturation taking place in the liquor as a result of the repeated absorption of SO_2 and the oxidation of the calcium sulphite formed. Methods for de-supersaturation were evolved, which are incorporated in the Howden—I.C.I. system* installed at Fulham and already in operation at the Tir John Power Station, Swansea.

In view of the immense fuel consumption of modern power stations, and the replacement by them of a multitude of uncontrollable point sources of pollution, the technical possibility of complete purification of their flue gas emission will prove to be an important step in the reduction of undesirable dispersoids in our atmosphere.

50 *Queen Anne's Gate,*
Westminster, S.W. 1.

* Pearson, Nonhebel and U'lander, *J. Inst. Fuel*, 1935, 8, 119.

GENERAL DISCUSSION.

Dr. R. Lessing, in introducing his paper, pleaded for precise definitions of the various types of dispersoids in gases. He considered that the outcome of this General Discussion would be of great value even if it only resulted in the acceptance of a reasoned nomenclature in the light of the papers submitted, quite apart from the subject-matter of the work itself.

Mr. A. G. Grant (*Darlington*) said: This paper covers a field too vast to be discussed adequately in so short a time, but our thanks are due to the author for his able review of industrial dispersions; the subject matter of the paper is, in fact, the *raison d'être* of the meetings. Apart from the more academic interest of dispersoid investigation, its main object is to evolve such an understanding of the nature and properties of suspended matter in gases as will allow of their effective avoidance or removal on the industrial scale. In few cases is it necessary artificially to produce a gaseous dispersion, whereas removal is an almost universal problem. I hope that some of us may be able to abstract and summarise the papers we have heard in the light of their industrial applications.

I would like to support Dr. Lessing in his plea for a standardised nomenclature. We have a plethora of rather vague terms—dust, mist, fog, haze, fume, and the like—and none has yet found a concise and accepted definition.

One regrets that no detailed work is reported on the formation and nature of tar fog, a dispersion of very great importance in the fuel industries,

and hopes that Dr. Lessing's reference will stimulate further basic investigation.

The occurrence of so-called gums in town's gas is an interesting case of an extreme dispersion in that the gum concentration is of the order of 10⁻⁶ grammes per cubic meter.

We require much more accurate knowledge regarding the electrical precipitation process. Investigation would fall broadly into two spheres :

- (a) The " pure electric " phenomena centring round the corona discharge in various gases and with various field shapes.
- (b) The dispersoid phenomena, which can be sub-divided thus :—
 - (1) The charging of dispersoid particles and the mode of their removal from the gaseous medium.
 - (2) The phenomena and their control arising from deposition of the dispersoid on the electrodes.

These problems are fundamental to the design and understanding of electrical precipitation plant. Whilst various contributions have been made towards their elucidation, the electrical precipitation process remains as one designed and operated largely on an empirical basis. Where mathematical relations are known, these are used for comparative and co-ordinating work rather than for basic design.

Mr. W. A. Damon (*London*) said : I am particularly interested in that part of Lessing's paper which deals with the contamination of the atmosphere by the carbonaceous dust loosely adhering to coal. If burned in the ordinary way, much of it will certainly be emitted to atmosphere, together with the flue gas and, if as is done in some places, it is dumped on the spoil bank, it will be very likely to initiate spontaneous combustion. Many of the burning pit banks which are so prevalent in the North of England are due to the indiscriminate dumping of excessive carbonaceous matter. Therefore, I am much in sympathy with his plea for combustion under conditions which allow of the collection of the ash.

Lessing says that of the mass of solid matter suspended in the air over any area about 15 per cent. will be deposited. How did he arrive at this figure, and what happens to the remaining 85 per cent. Presumably when a South wind blows, towns to the North of London suffer more from London's pollution than from their own.

Mr. C. H. Bosanquet (*Billingham*) said : Dr. Pearson and myself are partly responsible for Dr. Lessing's figure of 15 per cent. for the fraction of the total emitted particles caught in deposit gauges in London. He arrived, I believe, at the figure by comparison of the deposit gauge figures with the estimated total emission, and asked our opinion on the subject.

The equations developed in our paper lead to the expectation that in fine weather only about 10-20 per cent. of the particles of diameter 20 μ will be deposited in London, and an infinitesimal fraction of particles of the order 1 μ . The remainder will drift across Europe, becoming more dilute as the cloud diffuses upwards and sideways.

The fraction 15 per cent. probably represents the fraction of the time that it is raining, when nearly all particles will be brought down near their point of origin.

Dr. R. Lessing (*London*), in reply, said that the figure of 15 per cent. as the proportion of the total solid matter in London air settled or washed out by rain (as determined by the deposit gauges of the Atmospheric Pollution Committee) was an estimate at which he arrived taking all known factors into account. This was confirmed by Mr. Bosanquet on a mathematical consideration of the sedimentation of particles at average wind velocities.

TWENTY-FIVE YEARS' PROGRESS IN SMOKE ABATEMENT.

BY J. S. OWENS.

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The selection of a title for this paper was prompted by the fact that it was in 1912 the organised investigation into the degree of atmospheric pollution by smoke commenced. The starting-point of the investigation was very definite: At a conference held at an International Smoke Abatement Exhibition in London, the following resolution was moved by the author:—

“That in the view of this Conference it is desirable that immediate steps should be taken to decide upon and secure the general adoption of a standard method for the measurement of atmospheric pollution by smoke and other products of combustion and heat, in order that the data now being collected may possess a comparative value, and that a Committee be appointed to draw up details of a standard soot and dust-measuring apparatus and methods of its use.”

The original Committee continued its work on a voluntary basis for several years. A number of Municipal Authorities had by then associated themselves with the investigation, and a grant in aid of the expenses was obtained through the D.S.I.R. The Committee then functioned as an “Advisory Committee on Atmospheric Pollution” in association with the Meteorological Office and was subsequently attached to the Air Ministry. The work continued to expand and the control of the investigation ultimately passed to the D.S.I.R., in whose hands it now is.

In attempting a review of progress made since the initiation of the investigation, certain difficulties have to be recognised. We are not in the position of having uniformly distributed observation stations over the whole country, but there is rather a tendency to concentrate stations in the more highly polluted neighbourhoods. This is a perfectly natural result since such places are likely to be more concerned with the condition of their atmosphere than would be, for example, a sea-side resort far removed from any manufacturing area. However, one effect of this is that when attempting to estimate the condition of the air of this country as affected by smoke pollution, allowance has to be made for this concentration. One way of examining the changes which have occurred would be to take each station individually and compare the result obtained year by year, and this in some respects is the most satisfactory. In the case of large cities where a number of stations have been established, the average of the stations may be taken and, provided they retain the same position, may be compared with a view to finding what improvement, if any, has resulted.

In this paper the details of the methods adopted for measurement will not be dealt with, but rather the general results obtained. It may, however, be stated briefly that the measurement upon which most reliance is based is an estimation of the weight of matter deposited from

the air upon a measured area at or near ground level. A standard deposit gauge has been evolved for this purpose and is in use at about 100 different stations throughout the country.

In addition to the measurement of deposit, the suspended matter is also examined by a different method, *i.e.* by filtration through white paper leaving a stain which, in smoke-polluted cities, can be made to give a measure of the degree of pollution of the air by sooty matter.

The desirability of reviewing the progress made to date will be evident since it will be seen from what follows that the rate of improvement of the air of our cities is by no means as great as it should be, and the author hopes that the condition set forth in this paper will make it evident that greater efforts must be made in the direction of smoke abatement if we are to obtain any marked and continued improvement.

Since this investigation started there have been in operation 158 stations making official reports. These, however, have not all been in operation at the same time, nor have they all continued from the beginning until now. Hence it becomes necessary to make some selection of stations in examining the variation of the deposit. This has been done by excluding from the comparison any station with less than eight consecutive years' observations, except in one or two exceptional instances.

The reports made of deposited impurity show this analysed into soluble and insoluble matter, and experience has shown that the amount of rainfall in any year has a marked effect upon the amount of soluble matter deposited, but little effect upon the insoluble. Hence we must not compare individual years but rather find some method which will show the trend over a longer period of years. Again the insoluble matter deposited has been divided into tar, carbonaceous matter and ash, and the soluble into loss on ignition and ash, while the soluble matter has also had the amount of sulphates, chlorine and ammonia estimated.

In such an examination as this and in order not to burden the paper with too many figures it is advisable to select a few of the more important elements of the deposit for consideration. It has, therefore, been decided to compare upon the basis of total solids deposited from the atmosphere in any year, the deposit of sulphates found in the soluble matter and the amount of tar deposited. Before dealing with the individual stations, it might be well to give the reasons for this selection :—

The total solids deposited gives a gross measure of the pollution reaching the ground from the air, although it is not all derived from the smoke or grit from chimneys, it may at least be regarded as atmospheric pollution. Some of the deposited matter is undoubtedly derived from wind-blown dust, and hence it is found that the insoluble part of the deposit tends to be higher in summer than in winter, whereas the soluble part tends to be higher in winter than in summer.

The selection of sulphates deposited is based upon the fact that the main source of pollution of the atmosphere by sulphur is from the combustion of fuel containing sulphur. In addition, it is one of the most dangerous products and is injurious to health and vegetation as well as to building material; while, being derived from the combustion of fuel, it is some measure of the pollution from this source. Unfortunately the sulphate emitted from a chimney is in an invisible form and is, therefore, not eliminated by eliminating visible smoke. It follows also that efforts to attack visible smoke do not necessarily reduce the amount of sulphur pollution in the air, and it has to be dealt with independently by some of the methods recently adopted successfully in our large power stations.

Tar is pre-eminently a product of bituminous coal burnt in domestic

fires. Hence it is included as some measure of the degree of pollution by domestic smoke. It is well known that the soot from domestic smoke contains a high percentage of tar, often up to 30 per cent., whereas that from boiler furnaces or other well designed furnaces contains little or no tar.

The above reasons will explain why these three elements of pollution have been selected to give a reasonable measure of the progress made in the prevention of pollution of the air.

The stations examined are shown in the tables below for the years available and a brief summary of the position may now be given referring to the attached tables :—

In dealing with the progress of events, it will be best to take individual cities because the conditions in different cities vary very much, and it will be observed from the tables that, whereas in some cases there has been improvement, in others this is not the case.

London.—In this case the figures shown are an average for eight stations, and, as in all other tables, they represent the deposit from the air estimated in English tons per square mile. We have here a consecutive series of twenty years with no break, and these should give a very fair picture of the course of events. Starting at 1915/16 we find the deposit of total solid matter was 415 tons per square mile, 72 tons of sulphates and 4 tons of tar. Following this there was a fairly steady improvement until 1921/22, that is for seven years, and this improvement shows up as a reduction in total deposit and in deposit of sulphates. In this year 1921/22 the total deposit had fallen to 284 tons per square mile and the sulphates to 25 tons. In the following years between 1921 and 1935, the total deposit has altered very little, there have been some ups and downs, but it would not be very wrong to say that the conditions have remained practically unaltered. It is not quite so satisfactory when we look at the sulphates deposited, as here we find actually an increase, although not very great. So that while in 1921/22 there was a deposit of 25 tons, in 1934/35 this had increased to 49 tons per square mile, while tar remained unchanged. Here then we find a state of affairs which is not very easy to explain, but at any rate it can be said that there is no great ground for optimism as regards the condition of the air of London during the last fourteen or fifteen years.

Glasgow.—Here also we have an unbroken series of twenty years' observations, and the figures are an average of nine stations. In some respects it follows curiously the behaviour of London. In 1915/16 the total deposit was 422 tons per square mile, 92 tons of sulphates and 4 tons of tar. This diminished regularly until 1921/22 when we find a total deposit of 255 tons, and 34 tons of sulphates per square mile. Since then for the next fourteen years there have been some ups and downs but no general improvement can be observed. In 1934/35 the total deposit was 268 tons per square mile including 37 tons of sulphates, while tar remained unchanged.

The cause of this curious behaviour in the two cities is not by any means obvious, and may be a suitable subject for speculation and discussion at a meeting such as this.

Wakefield, W.R. Rivers Board.—This gauge is in the centre of the city in a manufacturing and residential area. There is a period of eleven years with one or two breaks which do not affect the sequence very much, and, so far as total deposit from the air and the deposit of sulphates are concerned, Wakefield shows a continuous improvement. The deposit in 1924/25, the first year available, amounted to 613 tons per square mile, while sulphates amounted to 136 tons and tar 8 tons. In 1934/35 this was reduced to 225 tons per square mile total deposit, 24 tons sulphates and 6 tons tar, a very creditable state of affairs.

Bournville Works.—This gauge is 4 miles S.W. by S. of Birmingham. There are ten years' consecutive records and a fairly constant history of

improvement, but not anything very spectacular. Starting in 1924/25 with 192 tons per square mile of total deposit, 17 tons of sulphates and 2 tons of tar, we finish in 1934/35 with 173 tons of total deposit, 18 tons of sulphates and 1 ton of tar.

Bournville Village.—This gauge is $4\frac{1}{2}$ miles S.W. of Birmingham in a residential area. Here we have nine years' records, and a slight improvement is also indicated. In 1925/26 the total deposit amounted to 157 tons per square mile, the sulphates to 18 tons and the tar to 1 ton, while in 1933/34 the figures had fallen to 93 tons per square mile of total deposit, 11 tons of sulphates and 1 ton of tar. This behaviour is somewhat similar to that of Bournville Works, it shows an improvement but not a very great one.

Birmingham Central.—There are ten years' records and again a history of improvement, but not very great. Starting in 1922/23 with a total deposit of 419 tons per square mile, sulphates 50 tons and tar 4 tons, we finish in 1931/32 with 340 tons per square mile of total deposit, 27 tons of sulphates and 4 tons of tar. This is a somewhat similar history to the Bournville records: This is for the centre of the city.

Cardiff.—This gauge is also in the centre of the city. We have nine years available at Cardiff, commencing at 1926/27 with a total deposit of 368 tons per square mile, sulphates 21 tons and tar 9 tons. This improved until 1930/31 when there was 133 tons total deposit, 22 tons of sulphates and 2 tons of tar. After that the improvement was not maintained, but with some ups and downs we arrive at 140 tons per square mile total deposit, 17 tons of sulphates and 1 ton of tar in 1934/35.

Gloucester.—This shows a fairly constant improvement for the nine years of which we possess records. It commences in 1926/27 with 343 tons per square mile total deposit and finishes in 1934/35 with 117 tons per square mile. In this case we have no record of sulphates or tar.

Leicester, Town Hall.—This gauge is less than $\frac{1}{2}$ mile S.S.E. of the centre of the city. There are only eight years' records here, commencing in 1927/28 with 370 tons per square mile total deposit, 42 tons sulphates and 3 tons tar. There was very little improvement noticeable until 1933/34 when there was a definite drop in the deposit, and in 1934/35 the total deposit amounted to 259 tons per square mile, sulphates 24 tons and tar 4 tons. We may rank this city as having improved at any rate during the last couple of years.

Newcastle, Westgate.—The gauge is approximately $\frac{1}{2}$ mile west of the centre of the city. We have ten years' observations commencing 1925/26, and a fairly constant history of improvement up to 1934/35. The total deposit amounted to 443 tons per square mile, the sulphates 69 tons and the tar 13 tons in 1925/26: these figures had fallen to 292 tons total deposit, 35 tons sulphates and 8 tons tar in 1934/35.

Newcastle, Town Moor.—This gauge is $1\frac{1}{2}$ miles north of the centre of the city in fairly open country. It has the same series of years and shows a somewhat similar history to that at Westgate, but not such a marked improvement. The total deposit in 1925/26 was 268 tons per square mile, the sulphates 45 tons and the tar 4 tons, while in 1934/35 these figures had dropped to 236 tons per square mile total deposit, 42 tons sulphates and 6 tons tar.

Rothamsted.—This gauge is 1 mile S.W. of Harpenden Town in open country in a residential district. Rothamsted is a country station which gets most of its pollution by drift from London or other cities. There are sixteen years' observations, and a definite improvement during this period although not a very constant one. In fact most of the improvement occurred in the first four years when the deposit fell from 245 tons in 1919/20 to 86 tons per square mile in 1922/23. There were ups and downs after this until 1934/35 when the total deposit was 83 tons per square mile. We may, therefore, say that the last twelve years show practically no improvement.

Rochdale, Technical School.—Here we have twelve records covering the years 1916/17 to 1927/28, and there is, on the whole, an evidence of reduction of deposit based upon the total solids. Starting in 1916/17 with 731 tons per square mile, we finish in 1927/28 with 584 tons.

To continue with the story of Rochdale, as the Technical School gauge did not continue beyond 1927/28, we have to use the records from another gauge, i.e. at the Town Hall, and while these figures must not be taken as representing the same conditions as held at the Technical School, they may be compared amongst themselves for improvement or otherwise. In the Technical School gauge the observations of sulphates and tar were not carried out, but these were estimated in the Town Hall gauge.

Rochdale, Town Hall.—This gauge is in the centre of a manufacturing city. We have a period of eight consecutive years' observations here, and if we base our conclusions on total solids the deposit drops from 350 tons per square mile in 1927/28 to 236 tons in 1934/35. The sulphates and tar, however, do not tell quite the same story, and as these are specifically combustion products, they are perhaps more reliable. Thus in 1927/28 there was a deposit of 38 tons of sulphates per square mile, and 4 tons of tar, while in 1934/35 the respective figures were 40 and 4, showing no improvement.

Burnley, Town Hall.—There are nine years' observations available here, and the station is very remarkable in the sense that a sudden improvement occurred after three years, and the low level was maintained subsequently. In 1925/26 the total deposit amounted to 860 tons per square mile, 117 tons of sulphates and 25 tons of tar. In 1927/28 the figures were respectively 856, 137 and 11. There was a sudden drop next year to a total deposit of 464 tons per square mile, sulphates 31 tons and tar 10 tons, and the condition remained more or less the same as regards total solids and sulphates until 1933/34, the final figures being total solids 427 tons per square mile and sulphates 31 tons. There was, however, a definite increase in the quantity of tar deposited, which, increased steadily up to 30 tons per square mile in 1933/34, an excessively heavy deposit. There is no obvious explanation of the sudden reduction in the amount of deposit, but the fact that it occurred simultaneously in the total solids and in the sulphates suggests that there was a definite reduction in the amount of smoke. This gauge is in the centre of the city in a manufacturing district.

The cities which show at least some improvement in the amount of deposit from the air have been dealt with first, and we will now examine those which show no improvement or a falling back.

Leeds, Headingley.—The gauge is in a residential area 3 miles from the centre of the city. We have twelve years of observations, and the history is not one of continuous improvement, but rather the reverse. Commencing in 1923/24 with 12 tons total deposit, 13 tons sulphates and 1 ton per square mile of tar, we finish in 1934/35 with 122 tons per square mile total deposit, 14 tons sulphates and 1 ton tar.

Leeds, Hunslet.—This gauge is in an industrial area $1\frac{1}{2}$ miles from the centre of the city. Here again we have thirteen years' records and somewhat the same story. There is practically no difference between the condition now and twelve or thirteen years ago. In 1922/23 the total deposit amounted to 305 tons per square mile, the sulphates to 25 tons and the tar to 5 tons. In 1934/35 the figures were 301 tons of total deposit, 23 tons of sulphates and 3 tons of tar per square mile.

Leeds, Park Square.—The gauge is $\frac{1}{2}$ mile from the centre of the city in a densely populated area. There are thirteen years' observations available, commencing 1922/23 when the total deposit was 305 tons per square mile, sulphates 29 tons and tar 5 tons. These figures have altered very little until 1934/35 when the total deposit amounted to 338 tons per square mile, the sulphates to 23 tons and the tar to 3 tons. Thus in the total impurities deposited in the air we find no improvement, but there is a slight improvement in the sulphates and tar.

Leeds, York Road.—This gauge is 1 mile from the centre of the city in a densely populated working-class district. Here we have twelve years' observations and the figures tell the same story as at Park Square. Commencing 1923/24 with a total deposit of 247 tons per square mile, 25 tons of sulphates and 3 tons of tar, we finish in 1934/35 with 292 tons of total deposit, 24 tons of sulphates and 4 tons of tar. Thus these stations in Leeds indicate no improvement in the condition of the atmosphere.

Liverpool, Netherfield Road.—The gauge is $1\frac{1}{2}$ miles N.N.E. of the Town Hall in a manufacturing and very thickly populated area. There are fourteen years' observations, starting in 1921/22 when the total deposit was 548 tons per square mile, sulphates 52 tons and tar 4 tons. Conditions have not improved since then, in fact there is evidently more pollution in the atmosphere, since the total deposit in 1934/35 was 590 tons per square mile, sulphates 66 tons and tar 5 tons.

Marple.—This gauge is in open country tending to become suburbanised. We have eleven years' observations at Marple commencing in 1924/25 with a total deposit of 102 tons per square mile, 38 tons of sulphates and 2 tons of tar. The total deposit shows no improvement during the following ten years, but sulphates and tar do show a reduction. The figures for 1934/35 were 105 tons per square mile of total deposit, 21 tons of sulphates and 1 ton of tar.

St. Helens.—The gauge is in the centre of the city. We have eighteen years' consecutive observations here commencing 1917/18 with 612 tons per square mile total deposit, 99 tons of sulphates and 13 tons of tar. These figures fell rapidly during the subsequent three years, and in 1920/21 the total deposit was 371 tons per square mile, the sulphates 59 tons and the tar 4 tons. After that the improvement was not maintained, but in some years, the conditions went back and in 1934/35 the total deposit amounted to 431 tons per square mile, sulphates 30 tons and tar 9 tons. Looking at the column of sulphates deposited here there is a period from 1927/28 to 1934/35 when there was a continuous reduction in the sulphates, this was not, however, reflected in the tar or total deposit.

Stoke-on-Trent, Leek Road.—This gauge is in the centre of the city in a manufacturing area. We have available eleven years' observations commencing 1924/25 and the position disclosed is not very satisfactory. In 1924/25 the deposit of total solids was 192 tons per square mile with 21 tons sulphates, while in 1934/35 this had risen to 232 tons of total deposit and 29 tons of sulphates. As will be seen there has been a gradual deterioration, not entirely continuous.

At Castleford, Garston and Edinburgh, where there are not a great number of years for comparison, the indications are of a fairly steady condition of impurity. There are slight variations from year to year, but hardly anything which can be regarded as evidence of improvement or deterioration.

We could thus divide the stations referred to in this paper into three groups, the first in which a definite improvement has been indicated in the degree of pollution of the air. This group includes London, Glasgow, Wakefield (W.R. Rivers Board), Bournville Works and Village, Birmingham Central, Cardiff, Gloucester, Leicester Town Hall, Newcastle (Westgate and Town Moor), Rothamsted, Rochdale (Technical School and Town Hall), and Burnley. In the second group there has been an equally definite deterioration. This group includes, Leeds (Headingley, Hunslet, Park Square and York Road), Liverpool (Netherfield Road), Marple, St. Helens, and Stoke-on-Trent (Leek Road), while the third group shows little or no change in the condition of the air and includes Castleford, Garston and Edinburgh.

It is necessary to remember that a certain selection has had to be made of the available stations for reference in this paper. It is hardly possible to give a definite answer to the general question "Is the

TABLES SHOWING THE AMOUNT OF IMPURITY DEPOSITED IN TONS PER SQUARE MILE (ANNUAL TOTAL).

Glasgow (Average of nine stations).				Liverpool, Netherfield Road.				London (Average of eight stations).			
Year.	Total Solids.	Sul-phates.	Tar.	Year.	Total Solids.	Sul-phates.	Tar.	Year.	Total Solids.	Sul-phates.	Tar.
1915/16	422	92	4	1921/22	548	52	4	1915/16	415	72	4
1916/17	380	89	4	1922/23	625	50	6	1916/17	400	68	4
1917/18	447	84	7	1923/24	645	61	7	1917/18	379	60	3
1918/19	386	77	3	1924/25	577	63	7	1918/19	372	70	3
1919/20	316	59	2	1925/26	635	78	0	1919/20	346	53	3
1920/21	322	42	5	1926/27	547	72	5	1920/21	307	27	5
1921/22	255	34	3	1927/28	557	70	6	1921/22	284	25	5
1922/23	254	38	2	1928/29	636	65	5	1922/23	302	30	3
1923/24	321	41	3	1929/30	552	64	7	1923/24	288	33	2
1924/25	284	51	3	1930/31	520	67	6	1924/25	319	41	3
1925/26	274	46	3	1931/32	520	70	6	1925/26	264	32	3
1926/27	284	43	3	1932/33	585	61	5	1926/27	303	40	4
1927/28	320	50	2	1933/34	522	53	5	1927/28	316	40	4
1928/29	263	38	2	1934/35	590	66	5	1928/29	255	29	4
1929/30	280	41	3	1935/36	683	57	6	1929/30	272	35	4
1930/31	278	39	3					1930/31	289	41	4
1931/32	252	37	2					1931/32	281	41	4
1932/33	232	33	2					1932/33	272	41	4
1933/34	230	27	4					1933/34	315	45	5
1934/35	268	37	3					1934/35	298	49	5
1934/36	239	28	3					1935/36	284	43	4

condition as to smoke pollution improving in this country or otherwise." It will be seen from what has already been said that improvement may be going on in one place and deterioration in another, and it would not be fair, for example, to take two such places and by averaging them conclude that the general condition was unaltered. It is true that the smoke emitted in any city is not confined to its own boundaries, but spreads over the whole country, and in this sense there is a general pollution of the air which might be estimated as distinct from the local pollution produced in a specific neighbourhood. Possibly the condition of Garston might be taken as representing this general rather than local pollution, since the station is situated well out in the country and produces little smoke pollution in its own neighbourhood.

The lesson to be learnt from the foregoing is fairly obvious: The fact that certain cities have reduced the pollution of their air very much is proof that it can be done with care and attention, and might be given as an answer to any doubts raised by other cities as to their ability to reduce smoke. The condition in this country at present is by no means satisfactory, and it is obvious that we should put a great deal more energy and effort into smoke prevention than we are doing. This might be taken as the lesson to be learnt from the cities of groups two and three. It is, however, not the cities only which suffer from the smoke pollution: it is astonishing the degree of pollution of the air in the open country to leeward of a great city such as London. The track of the smoke cloud extends for many miles down wind and the concentration of smoke is so great even in the open country under such conditions that far more attention should be given to it by Public Health Authorities. The

author has often experienced a dense smoke haze, easily visible in a room, at a distance of 12 miles S.W. of London. Given suitable conditions which impede the dispersion of the smoke cloud from the city, that is, a low wind velocity and an inversion of the vertical temperature gradient overhead, then the smoke drifts along with little reduction in its concentration. The author has seen on the coast of Devonshire a thick smoke haze through which the sun had a deep orange colour, and he has traced this haze to the manufacturing districts in the Midlands. This paper is, however, intended to be rather a review of progress since the beginning of the investigation than a pointing out of lessons, and indeed they are sufficiently obvious to need little indication.

GENERAL DISCUSSION.

Mr. C. F. Goodeve (*London*) said: In welcoming us to Leeds the Vice-Chancellor of this University expressed a hope that we would close our discussion in a happier frame of mind than we had commenced it and that, before many years, we would do something to relieve the irritations of housewives, etc. From the title of this paper one receives a certain amount of encouragement, but it is misleading. This adequate summary given by Dr. Owens shows conclusively that, except for a few cities during the five-year period from 1915, no reduction in any of the impurities deposited from the air has been found and, in a good many cases, there is a serious increase.

An important question for the consideration of this meeting is "What is being done, or what is proposed to be done, with regard to the situation?" We have an active society which carries on extensive propaganda work. We can only hope that it will receive increased support and that its efforts may produce some improvement.

There is also "The Atmospheric Pollution Research Committee." Their very interesting annual reports contain, amongst other things, the results of an enormous number of determinations of the deposits from the air in different cities in this country. The available statistics now cover millions of observations. Some years ago, I attempted to make a statistical analysis of these figures. Beyond showing what Dr. Owens has discussed in this paper, the results of this analysis were disappointing. Mr. Wilsdon, however, has persevered further and obtained a number of curves which are given in the last Report. In this connection, I should like to quote from his paper the following sentence (p. 51):—

"Whatever may be the true interpretation of the early data, it does not seem possible to advance much further by examination of existing records."

It would appear that Mr. Wilsdon agrees with me that the large amount of work involved in obtaining these statistics is not leading to any definite conclusions. These figures cover a period of twenty-one years. I would ask the members of this committee, most of whom are present, seriously to consider whether it is possible to direct some of the enormous amount of labour involved in obtaining these statistics along more useful lines.

I am not familiar with the terms of reference under which this committee is appointed, but I would venture to suggest that they might find practical means to help the situation by, for example, advising local authorities or even investigating for them the causes of atmospheric pollution. One finds in the reports for a number of years that unusually high deposits were found in the neighbourhood of Ravenscourt Park, London. I would like to ask the committee whether the cause of this high deposit was ever found and if so, were any steps taken to remove it.

The most encouraging aspect of the whole question comes from the amount of independent work which is being done by private companies for the improvement of atmospheric pollution. The London Power Company are among the pioneers in this work. When one considers the large amount of private consumption of coal which will be replaced by electricity produced from a practically pollution-free power station, one can appreciate that the Battersea Power Station will produce no small improvement in the conditions obtaining in London. In this connection, I would like to quote from Dr. Coste's paper to this discussion :

"Dust from leaves in Battersea Park, near the Power Station, was mostly domestic and horticultural in origin, very few spheres being found, showing the efficiency of the gas-washing plant."

In addition to the work of the London Power Company, there are also the highly successful experiments of Imperial Chemical Industries carried out at Billingham and described in Nonhebel's paper to this discussion. As a result of their work it is now possible to instal an efficient plant for the smallest of industrial chimneys. There remains no excuse for the pollution of the atmosphere by the small factory.

We all look forward to the opening of the Fulham Power Station in London and feel confident that it will be as successful as the others. There are also a considerable number of gas washing plants for power stations in various parts of the country, but the small factory is very slow in responding.

Aside from this independent work, we have little to satisfy our minds as to the future. Chemistry and engineering have solved most of the practical problems involved and the matter is now largely a political one. It is to be hoped that the civic authorities in this city will take a leading part and, before long, Leeds will lose its title of "The City of Perpetual Mourning."

Professor F. G. Donnan (*London*) said he thought that Mr. Goodeve's criticisms were unjustified. The Atmospheric Pollution Committee had done an immense amount of excellent work in devising methods of measurement and obtaining quantitative data. They could not be blamed for any failure on the part of Municipal and Government Authorities to take action.

Dr R. Lessing (*London*) pleaded for a survey of the sources of atmospheric pollution as distinct from the observation of the incidence and effects. For this purpose, a limited number of types of coal-consuming plants and appliances should be investigated. Whilst the total emission may not have been reduced in amount in the 20 years during which observations have been made, the character had changed, mainly in the direction of a diminishing soot and tar content and an increasing proportion of ash dust and coke particles.

Dr. G. M. B. Dobson (*Oxford*) said : As I have some responsibility for the work of the Atmospheric Pollution Research Committee, I should like to make some explanations in view of Mr. Goodeve's friendly criticisms of this work.

Firstly, it is entirely outside the scope of this Committee to initiate work on methods of reduction of smoke from either domestic or factory chimneys, or to test existing methods. Their work is to devise methods for the accurate measurement of the pollution existing in the air, and to advise local authorities of the best methods they should use in measuring the pollution in their towns. It is not even the duty of the Committee to make the routine observations of pollution all over the Kingdom, this being the duty of Local Authorities. In certain special cases the Committee do make observations, but their small income would have to be multiplied many times if they were to be responsible for all the observations now being made by the local authorities.

The Committee are responsible for advising what type of pollution should be measured, and it is entirely due to them that the method of measuring gaseous SO_2 was worked out by the Government chemist at

their special request, and at the expense of their funds. In this connection I would also mention that the question of the possible presence of droplets of H_2SO_4 has been much discussed by them, and the work which Mr. Coste (a member of the Research Committee) reported to this Conference, is a direct result of this. So far as I know, this is the first time an accurate measurement of the amount of H_2SO_4 in city air has been made, and the suggestion that a method had been worked out by the Government chemist several years ago but not used by the Committee is not correct.

Mr. G. Nonhebel (*Billingham*) said: The higher deposits of sulphates in Central London may well be due to the increasing use of coke for central heating in the office districts. Coke contains more sulphur in relation to its calorific value than coal, and the coal used for coking has usually in any case a higher sulphur content than best quality domestic coal.

With the growth of large centrally situated power stations there is now a strong case for the use of low pressure pass-out steam for heating in densely populated areas (particularly in towns like Leeds, where the domestic smoke from closely packed houses, often back to back, is so serious in the valleys) and close to one of the power stations. By this means a large proportion of the latent heat of the steam which is now lost in the condenser water would be saved.

For such a scheme to be tried, it would really be necessary to have a State-aided large-scale experiment, and to forbid the use of open fires in the district under investigation.

In New York City one of the central heating stations has a boiler output of 500 tons/hour. The visibility in this city is generally far better than that in London, owing to the absence of open domestic fires. The main problems there are, however, the elimination of grit and SO_2 from the chimneys of the large power stations, particularly in the Tudor City district where many of the buildings tower above the chimneys of two large power stations.

Dr. J. S. Owens (*London*), in reply (*communicated*): In reply to Mr. Goodeve's remarks, I would first refer to his last paragraph, in which he says that "chemistry and engineering have solved most of the practical problems involved and the matter is now largely a political one." This is really the heart of the whole question. If I might paraphrase Mr. Goodeve's statement, I would put it in this form: "So far as the prevention of smoke pollution from industrial processes is concerned, we are in a position to prevent this if we want to, and the continued existence of a polluted atmosphere from this cause is evidence of the lack of a sufficiently strong public desire to prevent it." This brings me to the suggestions as to the work of research on atmospheric pollution. I do not agree with Mr. Goodeve that the statistics obtained are not leading to any definite conclusion. The work done has shown clearly the degree of pollution of the air and the improvement which can, and has been affected in certain places. It will, I think, be generally accepted that if a problem like this is to be tackled, the first essential is some means of measuring, both to enable us to realise the extent of the evil and to indicate the degree of success attending efforts made to reduce it. The title usually applied to the work, that is "The Investigation of Atmospheric Pollution," is perhaps a little vague as to the specific nature of the investigation intended. The object in view was strictly one of measurement. Of course, this does not invalidate any criticism such as that another object should have been included, or might still be included, but the particular problem attacked was quite sufficient in view of the funds available.

In reply to the query as to the heavy deposits in Ravenscourt Park, London, the exact source of these deposits has not been found, nor have the Committee initiated any steps to remove it. This is a case, where such action would be outside the terms of reference of the Committee.

THE INFLAMMATION OF DUST CLOUDS.

BY R. V. WHEELER.

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A cloud of fine dust in air behaves in many respects similarly to a gas or vapour. If the dust is inflammable, its similarity to a gas in behaviour extends to its ability to propagate flame if it is present in sufficient concentration in the air.

Dusts vary in their degree of "inflammability" (*i.e.* in their ability to propagate flame when they form clouds in air) with their chemical composition and their fineness. It is not so easy to obtain a direct measure of the inflammability of a dust as it is of a gas or vapour. It is not easy, for example, to determine accurately the dilution limits (lower and upper) such as are usually sufficient to define the inflammability of a gas or vapour.

An indirect measure of the inflammability of a dust can be obtained by making use of the fact that the admixture with it of a sufficient quantity of an incombustible dust (stone dust) can render it incapable of propagating flame. Such a measure has been used more particularly for assessing the relative inflammability of coal dusts, mainly because a practical method of rendering harmless the dust produced during coal-mining is to treat it with stone dust. Two examples of the problems studied regarding the inflammability of coal dusts will be considered: (1) The effect of the concentration of the dust (of constant composition and fineness); and (2) the effect of the fineness of the dust (of constant composition and concentration).

The Effect of the Concentration of the Dust on its Inflammability.

The method of experiment used was, briefly, to determine the amounts of a chosen stone dust, intimately mixed with the coal dust and of the same degree of fineness, required just to prevent the continued propagation of flame when the mixtures were strewn along an explosion gallery and ignited by a standard source of ignition.

The explosion gallery was constructed of steel tubing 4 ft. in diameter, and was 325 ft. long. It was closed at one end. A known quantity of an intimate mixture of coal dust and stone dust (Fuller's Earth), prepared by hand from materials pulverised so that between 80 and 85 per cent. could pass through a 200-mesh (I.M.M. standard) sieve,* was spread evenly on the floor of the gallery. The means of ignition was a blown-out shot of 20 oz. of gunpowder, tightly stemmed with 8 in. (1 lb.) of coal dust. The shot was fired from a small cannon with a 2-in. bore placed on the floor of the gallery at a distance of 15 ft. from the closed end, with its muzzle pointing towards the open end. An open-ended steel tube, 1 ft. in diameter and 6 ft. long, was arranged immediately in front of, and in line with, the cannon. A quantity of the dust mixture to be tested, such that there were 1½ lb. of coal dust (irrespective of the proportions of coal dust and stone dust in the mixture), was strewn evenly within this tube.

* Throughout this paper, the meshes of sieves referred to are I.M.M. standard.

A series of tests with a number of loadings of a chosen coal dust was made, different proportions of stone dust being used at each loading until two mixtures were found of which one propagated flame throughout the gallery and the other, containing $2\frac{1}{2}$ per cent. more stone dust, merely extended the flame of the cannon-shot by 75 to 175 ft.

The results of crucial experiments with a coal dust of average inflammability are recorded in Table I.

TABLE I.—THE EFFECT OF THE CONCENTRATION OF COAL DUST ON ITS INFLAMMABILITY.

Expt. No.	Composition of Mixture per Cent.		Concentration in Gallery (oz. per cu. ft. of gas).		Result Length of Flame.
	Coal Dust.	Stone Dust.	Mixed Dusts.	Coal Dust.	
716	40	60	0.60	0.24	75 ft.
748	40	60	0.65	0.26	75 ft.
724	42.5	57.5	0.50	0.21	75 ft.
746	42.5	57.5	0.50	0.21	75 ft.
723	42.5	57.5	0.55	0.23	Throughout
715	42.5	57.5	0.60	0.255	Throughout
720	42.5	57.5	0.65	0.28	Throughout
710	42.5	57.5	0.70	0.30	125 ft.
747	42.5	57.5	0.70	0.30	175 ft.
727	45	55	0.90	0.405	Throughout
749	45	55	1.00	0.45	150 ft.
754	45	55	1.00	0.45	125 ft.
750	47.5	52.5	1.55	0.74	Throughout
752	47.5	52.5	2.20	1.045	Throughout
753	47.5	52.5	3.00	1.425	Throughout
731	50	50	0.30	0.15	100 ft.
744	50	50	0.30	0.15	75 ft.
738	50	50	0.35	0.175	Throughout
742	100	nil	—	0.05	125 ft.
743	100	nil	—	0.05	150 ft.
739	100	nil	—	0.075	Throughout

For the concentrations of dust recorded in this table in ounces per cubic foot capacity of the gallery, the assumption is made that all the dust strewn on the floor of the gallery was raised in suspension in the air either by the concussion produced by the cannon-shot or during the subsequent propagation of flame. The results are shown graphically in Fig. 1. The "upper limit" of concentration for this coal dust was not obtained. No experiments were made with concentrations of coal dust higher than 1.425 oz. per cubic foot of air. This concentration, for a mixture containing 52.5 per cent. of stone dust, amounts to about $2\frac{1}{2}$ lb. of mixture per linear foot of the gallery and such quantities as would be required to reach the upper limit, judging by the slope of the curve in Fig. 1, would have presented considerable obstruction in the gallery.

During an experiment in which the loading of dust along the gallery was initially heavy, the concentration of dust in the air was probably neither initially uniform nor continuously maintained as the flame travelled but was affected by the degree of turbulence created ahead of the flame. The initial inflammation might raise the whole of the dust as a dust cloud and the flame, after travelling a short distance, might begin to slacken speed by reason of the cooling action of the large excess of dust. The checking of the flame in this manner would reduce the amount of turbulence ahead of it and much of the dust would fall out of suspension in the air, leaving a concentration more favourable to the propagation of

flame. It was noted that the progress of flame along the gallery when it had been heavily loaded with dust was slow and spasmodic.

The "lower limit" of concentration of this coal dust (under the conditions of test) was about 0.07 oz. per cubic foot of air, and the optimum concentration, which was sharply defined, was 0.23 oz.

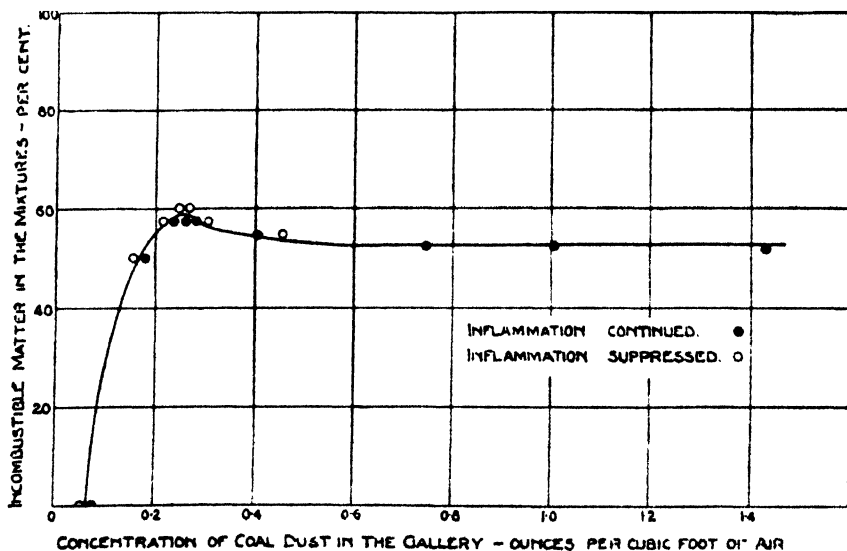


FIG. 1.—The effect on its inflammability of the concentration of coal dust in air.

With a coal dust of low inflammability by reason of its chemical composition, the amount of stone dust required to suppress inflammation, even at the optimum concentration, is small. Such a coal dust was therefore used in a series of experiments designed to test the possibility of determining an upper limit of concentration. The results are recorded in Fig. 2.

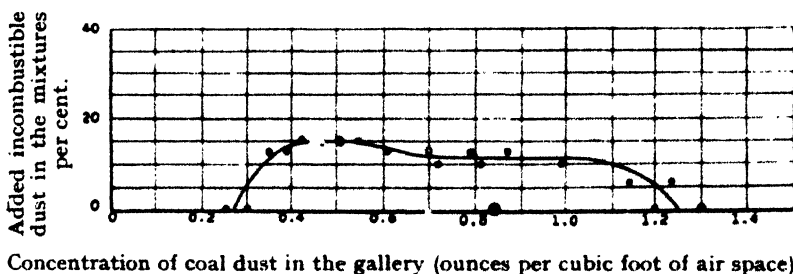


FIG. 2.—The effect on its inflammability of the concentration of coal dust in air.

An analogy can be drawn between these experiments and gaseous inflammations. Thus, Coward and Hartwell¹ have determined the limit of inflammability of firedamp in atmospheres containing carbon dioxide. Their results are shown graphically in Fig. 3, where the concentration of methane in the air is plotted against the concentration of carbon dioxide required to suppress inflammation. The concentrations of the gases are expressed as percentages by volume.

¹ *Safety in Mines Research Board Paper, No. 19.*

The Effect of the Fineness of the Dust on its Inflammability.

The physical quantity that measures the fineness of a particle of coal dust most significantly with respect to its reactivity, and thus with respect to its inflammability, is its specific surface, *i.e.* the ratio of its surface to its mass. Sufficiently accurate (relative) values for the specific surface of coal dust samples can be decided from their sieving analyses, whereby the proportions of particles of different sizes are measured.

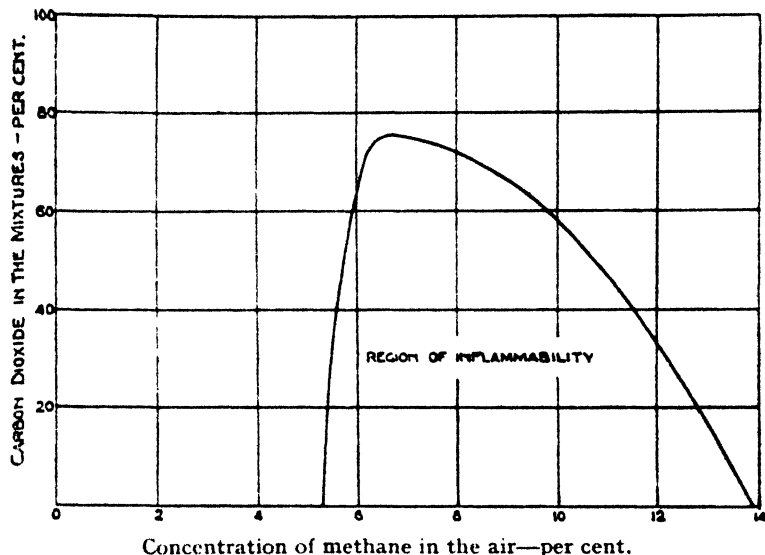


FIG. 3.—The effect on its inflammability of the concentration of methane in air.

Tests of the effect of the fineness of a coal dust on its inflammability were made in a similar manner to those on the effect of its concentration, using a coal which was as inflammable (by reason of its chemical composition) as that used for the experiments recorded in Table I. The stone dust used was, as before, Fuller's Earth, 85 per cent. of which would pass through a 200-mesh sieve, and all the tests were made with the optimum concentration of coal dust.

TABLE II.—THE EFFECT OF THE FINENESS OF COAL DUST ON ITS INFLAMMABILITY.

Preparation.	Sieving Analysis, per Cent.							Index of Inflammability.	
	3-5.	5-8.	8-20.	20-50.	50-100.	100-200.	Through 200.	Stone Dust, S, per Cent.	Ratio 100/(100-S).
A.	—	—	—	—	1	14	85	62.5	2.67
B.	3	7	6	4	2	13	65	55	2.22
C.	—	—	3	16	23	22	36	50	2.00
D.	—	—	4	33	13	14	36	45	1.82
E.	8	17	13	10	4	10	38	42.5	1.74
F.	—	—	29	21	7	11	32	40	1.67
G.	—	—	40	29	11	9	11	17.5	1.21
H.	8	22	24	19	8	7	12	15	1.18
J.	12	29	23	16	6	6	8	5	1.05

Nine preparations of the coal were made, to provide dusts of different degrees of fineness, by the use of coarse and fine grinding in different mills and by blending the products. Table II. records sieving analyses of these preparations, together with their "inflammabilities" expressed (a) as percentages of stone dust, S, in the mixtures through which (at optimum concentration) flame just failed to propagate when tested in the explosion

TABLE III.—FINENESS FACTORS FOR SIEVED FRACTIONS OF COAL DUST.

Mesh of Sieve.	Width of Mesh. Inch.	Mean Diameter of Particle (D). Inch.	Fineness Factor, $\left(\frac{0.00375}{D}\right)$.
3	0.1667		
5	0.1000	0.1333	0.028
8	0.0625	0.0813	0.046
20	0.0250	0.0438	0.086
50	0.0100	0.0175	0.214
100	0.0050	0.0075	0.500
200	0.0025	0.00375	1.000

gallery, and (b) as the ratios $100/(100 - S)$, which show the amounts of mixed coal dust and stone dust which unit quantity of coal dust just failed to render inflammable. The use of the latter index greatly simplifies discussion of the relationship between fineness and inflammability.

From general inspection of Table II. it is evident that the inflammability of a coal dust is affected in a marked degree by the proportion of through

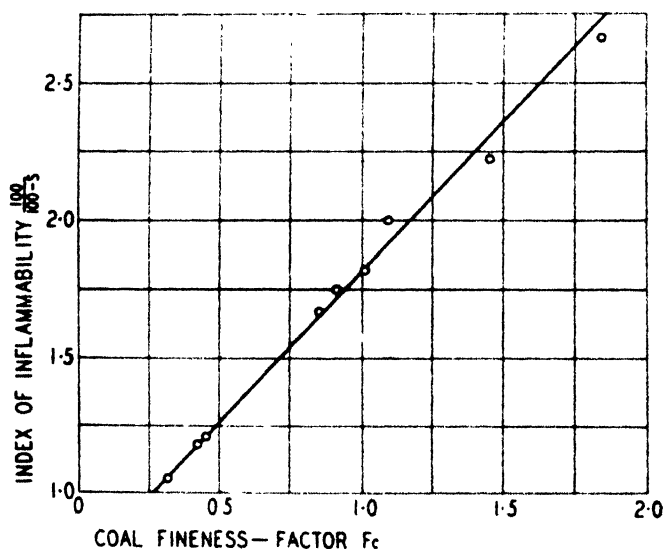


FIG. 4.—Relationship between fineness and inflammability.

200-mesh dust that it contains. The results of the tests with Preparations G, D and E, which contained nearly the same proportion through 200-mesh, show also that as the total amount of through 50-mesh dust is decreased the inflammability decreases.

Assessing the Fineness of the Dust Preparation.— It can be assumed that the speci-

fic surface of a dust particle is inversely proportional to its mean diameter, and that the average mean diameter of the particles in a sieved fraction is the mean of the widths of the two meshes between which the fraction lies. A proportional factor can then be assigned to each sieved fraction of a dust preparation, except that which passes through the finest sieve. To that fraction an arbitrary factor must be assigned. This method has been used to assess the relative fineness of the preparations used for the tests of

inflammability. The factors used for each sieved fraction are recorded in Table III.

With these factors for each sieved fraction, together with an arbitrary value 2.000 for the fraction passing through a 200-mesh, the composite fineness factor, F_s , for each of the dust preparations has been calculated from its sieving analysis, as shown in Table IV.

TABLE IV.—THE FINENESS FACTORS (F_s) OF THE COAL DUST PREPARATIONS.

Preparation.	3-5 (0.0028).	5-8 (0.046).	8-20 (0.086).	20-50 (0.214).	50-100 (0.500).	100-200 (1.000).	Through 200 (2000).	Fineness Factor F_s .
A.	—	—	—	—	0.005	0.14	1.70	1.85
B.	0.001	0.003	0.005	0.009	0.010	0.13	1.30	1.46
C.	—	—	0.003	0.034	0.115	0.22	0.72	1.09
D.	—	—	0.003	0.071	0.065	0.14	0.72	1.00
E.	0.002	0.008	0.011	0.021	0.020	0.10	0.76	0.92
F.	—	—	0.025	0.045	0.035	0.11	0.64	0.86
G.	—	—	0.034	0.062	0.055	0.09	0.22	0.46
H.	0.002	0.010	0.021	0.041	0.040	0.07	0.24	0.42
J.	0.003	0.013	0.020	0.034	0.030	0.06	0.16	0.32

In Fig. 4 the factors F_s for the preparations are plotted against their inflammability indices, $100/(100 - S)$. The graph shows a linear relationship which can be expressed by the formula: $100/(100 - S) = 1.1 F_s + 0.7$, whence $S = 100 - 100/(1.1 F_s + 0.7)$.

Any deviation from the relationship expressed by this formula is within the limits of experimental error of 2.5 per cent. stone dust for the determination of inflammability.

THE SPREAD OF SMOKE AND GASES FROM CHIMNEYS.

By C. H. BOSANQUET, M.A., AND J. L. PEARSON, B.A., PH.D.

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I. Introduction.

The authors have dealt elsewhere¹ with the following theoretical and practical aspects of the spread of chimney emissions:—

- a physico mathematical analysis of the phenomena involved in eddy diffusion;
- space-concentration distribution and mass-over-area distribution of emission from point and from line sources;
- the effects of chimney height on space-concentration and mass-over-area distributions.

Mass-over-area distribution of atmospheric pollution from chimney emissions is of practical importance, since it determines:—

- in rainy weather, the amount of acid and dust brought down by the rain,
- in fine weather, the extent of the curtailment of sunshine and ultra-violet rays.

¹ *J. Inst. Elec. Eng.*, July, 1935, and *J. Inst. Fuel*, April, 1935.

Space-concentration distribution governs the general environment of pollution, to which buildings and people are subjected when it is not raining, the effects from acids being dependent on and those from dust being largely independent of humidity. In a sense, ground level concentrations should not be of great practical importance, since, in any civilised community, they are presumably already maintained below the extent to which they become actively inimical to health or injurious to vegetation.

In this paper the mathematical analysis of the phenomena involved in eddy diffusion is carried further, with results that indicate that :—

- (a) any reasonable theoretical treatment of the subject-matter, utilising any reasonable assumptions, leads to closely identical conclusions carrying similar practical implications ;
- (b) the earlier and more general treatment of the subject, as mentioned above, presents a fairly correct picture of the mechanism and effects of eddy diffusion, and is reasonably consistent with ascertained facts and experimental data.

This paper, however, presents a more acceptable theory concerning vertical diffusion.

It should be noted that, in practice, no theoretical assumptions at all have to be made in order to determine :—

- (a) the mass-over-area distributions from continuous emission by point or line sources, as averaged over long intervals of time, say a year ;
- (b) similar distributions over short intervals of time when the wind is swinging, to and fro, through an angle of the same order as that of the cone of discharge.

With regard to distant ground concentrations arising from sources of continuous emission and as averaged either over long periods of time or over shorter periods with average wind swing, the only assumption is that concerning the effects of vertical diffusion. Up to distances of, say, fifteen chimney heights from the source, there can be little doubt about the ground concentrations, owing to the emission taking a form which is so often visible.

The authors wish to call attention, in particular, to the widespread misconceptions that have existed in the past concerning :—

- i. chimney height : It can now be clearly shown that any increase above a reasonable height has no practical effect.¹
- ii. concentration at moment of emission : This is really of very little importance indeed in practice, the most important factor in the problem of atmospheric pollution being the mass rate of emission of the objectionable constituents for any and every particular case.

II. The General Case of Eddy Diffusion (i.e. for a single Dispersing Cloud).

In a wind gases and dust will be dispersed more rapidly than in still air, since eddy diffusion arising from the effects of turbulence in the dispersing medium will be superimposed on the effects of kinetic diffusion and Brownian motion. Eddy diffusion coefficients found in practice vary considerably, but, in all cases, they are very large compared to the ordinary coefficients of the kinetic theory. The effects of these latter can be neglected in comparison.

In eddy diffusion the variations of velocity from place to place correspond to velocities of agitation, and the average distance an

¹ For a suggested criterion of reasonable height see *J. Inst. Elec. Eng.*, July, 1935.

individual portion of gas moves before losing its sense of direction corresponds to the free path.

G. I. Taylor³ has shown that there is no need to postulate anything definite about the type of motion of individual portions of gas in order to investigate the spreading of such properties as composition and momentum. All that is necessary is to assume that the correlations at different times between the vector velocities and the properties of the portion of the gas are functions of the time difference, the correlation decreasing from unity to zero with increasing time difference. The following analysis differs considerably from his, but is based on the same fundamental ideas.

Consider a gas in which a property C varies along the x axis. Let the root-mean-square velocity fluctuations of individual portions of gas be u . Let v be the velocity component along the x axis, and let $F(t)$ be the correlation between the values of v of the same portion of gas at times differing by t . Also, if the value of C varies from one portion of gas to another, let the correlation between the deviations of C from the mean of the surroundings at times separated by t be $f(t)$. If $f(t)$ is independent of the deviation from the mean, then the probable deviation will decrease by equal percentages in equal time, so that

$$f(t) = e^{-Kt}.$$

Consider the case of a portion of gas whose velocity component along the x axis at the zero of time is v . At time $-t$ let it be in a region where the mean value of C is C_0 , then when $t = 0$ the probable value of C of the portion considered is given by:—

$$\int_0^\infty K C_t e^{-Kt} dt \quad . \quad . \quad . \quad . \quad (1)$$

At time $-t$ the probable value of dx/dt is equal to $vF(t)$, so that the probable value of x is:—

$$x_0 - v \int_0^t F(t) dt,$$

and the probable value of C_t is therefore:—

$$C_0 - v \frac{dC}{dx} \int_0^t F(t) dt \quad . \quad . \quad . \quad . \quad (2)$$

Combining equations 1 and 2, the probable value of C can be found as a function of v . If for instance, $F(t) = e^{-Lt}$ then the probable value of C will be:—

$$C_0 - \frac{v}{K+L} \cdot \frac{dC}{dx} \quad . \quad . \quad . \quad . \quad (3)$$

This leads to a diffusion coefficient

$$D = \frac{u^2}{3(K+L)} \quad . \quad . \quad . \quad . \quad (4)$$

Any assumptions as to the form of $f(t)$ and $F(t)$ will yield an expression of this type. D is proportional to u^2 divided by the sum of two terms, K a rate of mixing term, and L a rate of loss of momentum term. K is obviously proportional to D and L is proportional to the effective kinematic viscosity of the gas. Now the kinematic viscosity is the diffusion

³ *Proc. Lond. Math. Soc.*, 1922, 20, 196.]

tend to increase as u increases. Hence, both u and $\int_0^\infty \phi(r) dr$ increase with the size of the cloud.

The problem can also be dealt with by dimensional analysis. The diffusion coefficient can be assumed to depend only on :—

the wind velocity	v
the kinematic viscosity	ν
some undefined length	l

The kinematic viscosity here is the ordinary kinematic viscosity, not the kinematic eddy viscosity. l may be the height above ground, the mean radius of the cloud, the distance the cloud has drifted from its source, or some kind of weighted mean of all three. In any case, the relation must hold that

$$D = \nu l f\left(\frac{\nu l}{\nu}\right) \quad (6)$$

If $D \propto \nu$, as suggested above, then $f\left(\frac{\nu l}{\nu}\right)$ must be a constant, it is also a matter of common experience in hydraulics and aero-dynamics that large scale phenomena are uninfluenced by viscosity, leading to the same conclusion.

It can therefore be assumed that D is very nearly proportional to νl for phenomena on a meteorological scale.

If the standard deviation σ be defined as the root-mean-square of the displacements of the constituents of a cloud from a plane passing through the centre of gravity and normal to the direction in which diffusion is being considered, then by the ordinary laws of diffusion

$$\frac{d\sigma}{dt} = \frac{D}{\sigma}.$$

If a cloud has its origin at ground level, and cross-sections of the cloud after drifting different distances downwind are similar then \bar{z} , the mean height above ground, is proportional to σ . If, therefore, l can be identified with σ or \bar{z} , and if $D \propto \nu$, it can be seen that $d\sigma/dx$ is constant where x is the distance the cloud has drifted from the source. Thus x , \bar{z} and σ are all proportional to each other, and it makes no difference except to the numerical constant which of them is identified with l .

This analysis leads to the conclusion that $\sigma \propto x$. Now, the cross-section of a cloud from a continuous point source such as a chimney is proportional to σ^2 , so that the mean density in such a cloud varies as the inverse square of the distance from the source. It is shown by Sutton⁴ that an inverse square law of decrease of density is a limiting case corresponding to perfect correlation between the motions of a portion of air at all times. He gives evidence, however, to show that the law is very closely approached in practice, so that variations of the turbulence of the air with weather conditions and with the nature of the ground will probably cause far greater errors in calculated values of the mean cross-section of a cloud at various distances than will a small deviation of π from unity in the formula $D \propto \sigma^2$.

III. Diffusion of a Gas Constituent from a Continuous Line Source.

A. In deriving a formula for the concentration of flue gas in the atmosphere at different points downwind from a chimney, it is convenient to treat the horizontal and vertical diffusions separately. The two diffusions will follow rather different laws owing to the effect of the ground, so that vertical diffusion takes place in a semi-infinite space instead of an infinite space.

Consider first a continuous line source of atmospheric pollution such as a row of chimneys, which is long compared to σ .

It can be seen by watching a persistent smoke cloud coming from a chimney that, at points a few chimney heights away downwind, the cloud sometimes appears to be in contact with, and sometimes rises clear of the ground. It is necessary, therefore, to consider either the maximum instantaneous pollution density at a point or else the average over a time long compared with the time of passage of an eddy. This long time average will be considered here.

In this case it is necessary to take account of vertical movements of the centre of gravity of the cloud as well as of the spreading of the cloud, since the average concentration at any point is equal to the product of the average concentration when the cloud overlaps the point and the fraction of the total time during which overlap occurs. For a cloud whose sinuosities are large compared to its diameter, the average concentration inside the cloud varies inversely as the square of the diameter and the time varies almost directly as the square of the diameter, so that the time average depends almost entirely on the amplitude of the sinuosities, and is nearly independent of the actual diameter of the cloud. The diffusion coefficient in the vertical direction then depends only on the root-mean-square of the vertical component of the wind velocity and on $\phi(r)$. These are both independent of the presence or absence of the cloud, so that D must be independent of both x and σ , and l must therefore be identified with z , the height of the point above ground.

The diffusion equation can therefore be written

$$D = p\sigma v \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where p is a numerical constant.

If diffusion can be neglected in the horizontal plane, *i.e.* if the source is a line source giving no cross wind variation of C , and if the concentration gradient in the direction of the wind is small compared to the vertical concentration gradient, then :—

$$\frac{dC}{dt} = pv \frac{d}{dz} \left(z \frac{dC}{dz} \right),$$

$$\text{or} \quad \frac{dC}{dx} = p \frac{d}{dz} \left(z \frac{dC}{dz} \right) \quad . \quad . \quad . \quad . \quad (8)$$

It appears an extraordinary conclusion at first sight that the diffusion coefficient should be least near the ground where the turbulence is expected to be greatest; however, the effect of the ground is to reduce the correlation between values of velocities at neighbouring points, *i.e.*

to reduce $\int_0^\infty \phi(r) dr$. Further, components of velocity normal to a surface must vanish at that surface.

B. Derivation of a Formula for Concentration at Ground Level due to a Line Source at Finite Height.

If a line source situated at a height h above ground emits a mass M of some constituent per unit length in unit time, then if the wind velocity is v at all points

$$\int_0^\infty C dz = \frac{M}{v} \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Combining equations 8 and 9, a complete solution can be obtained for the special case $h = 0$ in this case ;

$$C = \frac{M}{pux} e^{-\frac{z}{px}} \quad . \quad . \quad . \quad . \quad . \quad (10)$$

In the general case, it is possible to analyse the distribution in the plane $x = 0$ into a series of exponentials similar to a Fourier series, so that the combined effect of a number of positive and negative line sources at ground level, at points upwind of the actual source, will combine to produce a line source of strength M at height h in the plane $x = 0$.

If the virtual sources are of strengths A, B, C , etc., situated at $x = -d$, $x = -d/2$, $x = -d/3$, etc., then the conditions to be satisfied are :—

$$A + B + C + \dots = M$$

$$C = \frac{1}{pvd} \left(A e^{-\frac{z}{pd}} + 2B e^{-\frac{2z}{pd}} + 3C e^{-\frac{3z}{pd}} + \dots \right) \rightarrow 0,$$

when z is unequal to h .

These conditions are satisfied if $\frac{pd}{h}$ is vanishingly small and

$$A = M e^{\frac{h}{pd}}$$

$$B = -\frac{M}{2!} e^{\frac{2h}{pd}}$$

$$C = \frac{M}{3!} e^{\frac{3h}{pd}}$$

$$\text{If } \frac{h-z}{pd} = \psi.$$

Then

$$C = \frac{M}{pvd} e^{\psi - \psi^2}.$$

This expression is obviously vanishingly small for moderately large positive or negative values of ψ , and as d is decreased indefinitely, the distribution approaches more and more closely to a line source at height h .

For positive values of x :—

$$C = \frac{M}{pux} \left\{ \frac{e^{\frac{1}{p} \left(\frac{h}{d} - \frac{z}{x+d} \right)}}{1 + \frac{d}{x}} - \frac{e^{\frac{2}{p} \left(\frac{h}{d} - \frac{z}{2x+d} \right)}}{2! \left(1 + \frac{d}{2x} \right)} + \frac{e^{\frac{3}{p} \left(\frac{h}{d} - \frac{z}{3x+d} \right)}}{3! \left(1 + \frac{d}{3x} \right)} - \dots \right\} \quad (11)$$

The only place where the value of C is important is ground level, so that the special case of $z = 0$ will be considered.

Let
$$u = e^{\frac{h}{pd}}.$$

Then
$$d = \frac{h}{p \log u}.$$

Substituting this value in equation 11, and expanding the series in powers of u and $\frac{d}{x}$ gives:—

$$C = \frac{M}{pux} \left\{ \left(u - \frac{u^2}{2!} + \frac{u^3}{3!} - \dots \right) - \frac{h}{px \log u} \left(u - \frac{u^2}{2 \cdot 2!} + \frac{u^3}{3 \cdot 3!} - \dots \right) + \frac{h^2}{p^2 x^2 \log^2 u} \left(u - \frac{u^2}{2^2 \cdot 2!} + \frac{u^3}{3^2 \cdot 3!} - \dots \right) - \dots \right\}.$$

C is given by the limit of the sums of these series when u tends to infinity.

The sum of the first series is obviously $1 - e^{-u}$, and if each series be divided by u and then integrated with respect to u the result is the succeeding series.

The sums of the series for large values of u are therefore equal to:—

$$1, \log u + K, \frac{\log^2 u}{2!} + K \log u + L, \text{ etc.}$$

Where K, L , etc., are numerical constants.

$$\begin{aligned} \therefore C_0 &= \frac{M}{pux} e^{-\frac{h}{px}} \left(1 - \frac{Kd}{x} + \dots \right) \\ &= \frac{M}{pux} e^{-\frac{h}{px}} \quad \dots \quad \dots \quad \dots \quad \dots \quad (12) \end{aligned}$$

since d is vanishingly small.

C_0 is a maximum when $x = \frac{h}{p}$, and when x is large compared to $\frac{h}{p}$, the exponential term becomes unity, and C falls off inversely as the distance.

C. The General Case where $D = pux^n$.

Comparison of equations 10 and 12 shows that the value of C at ground level due to a source at height h is the same as the value at height h due to a source at ground level. This is also obviously true for a diffusion coefficient independent of height, and may be assumed to be generally true for any law of diffusion.

The general equation:—

$$\frac{dC}{dx} = p \frac{d}{dz} \left(x^n \frac{dC}{dz} \right)$$

can be solved for a source at ground level, so that if the above theorem be used

$$C_0 = \frac{2-n}{\Gamma\left(\frac{1}{2-n}\right)} \cdot \frac{M}{v(px)^{\frac{1}{2-n}}} e^{-\frac{h^{2-n}}{px}} \quad \dots \quad (13)$$

The maximum value of C occurs when $px = (2-n)h^{2-n}$, and the maximum concentration varies between $0.48 \frac{M}{vh}$ for $n=0$ and $0.37 \frac{M}{vh}$ for $n=1$.

The value of the concentration at the maximum is thus seen to be almost independent of the law of variation of diffusion with height and quite independent of the value of the turbulence constant p .

IV. Diffusion of Dust from a Continuous Line Source.

Equation 12 is derived on the assumption that no matter is lost from the cloud, and that gravity is without effect. In the case of dust particles, a steady fall must be superimposed on the dispersion, and all particles which strike the ground will be assumed to be retained. The result of this will be that the total mass of the cloud will decrease with distance.

Again, consider the case of an infinite line source of strength M , and let the free falling speed of the particles be equal to f .

The diffusion equation now becomes :—

$$\frac{dC}{dx} = p \frac{d}{dz} \left(z \frac{dC}{dx} \right) + \frac{f}{v} \cdot \frac{dC}{dz} \quad . \quad . \quad . \quad (14)$$

and

$$\frac{d}{dx} \int_0^\infty C dz = - C_0 \frac{f}{v} \quad . \quad . \quad . \quad (15)$$

Equation 14 is equation 8 with a term added to allow for the fall of the particles, and equation 15 gives the rate of loss of mass from the cloud due to the settling out of the particles.

If the source is so distant that the effect of height of emission is negligible, the solution of these equations is :—

$$C = \frac{A}{x^{1 + \frac{f}{pv}}} e^{-\frac{z}{pz}} \quad . \quad . \quad . \quad (16)$$

In the case of a gas $f = 0$, and for a very distant source C and C_0 are expressed by equations 10 and 12 respectively for a source at height h at any distance. The formula for the case of dust must be of the same type as that for a diffusing gas, since the latter is a limiting case of the former. At small distances from the source, the falling of the dust will tend to increase the ground concentration, and at great distances the reduction of total mass of the cloud will cause it to fall below that given by the gas formula.

If the ground concentration is independent of f at a distance X , then a possible form of the formula is

$$C_0 = \frac{MX \frac{f}{pv}}{pux^{1 + \frac{f}{pv}}} e^{-\frac{h}{pz}} \quad . \quad . \quad . \quad (17)$$

Since all the dust will eventually settle, and the amount settling on unit area in unit time is equal to $C_0 f$, we have the relation

$$\int_0^\infty C_0 f dx = M.$$

If f/pv is small, this condition is satisfied by equation 17 if $X = 1.78 \frac{h}{p}$. then

$$C_0 = \frac{M \left(1.78 \frac{h}{p} \right) \frac{f}{pv}}{pux^{1 + \frac{f}{pv}}} e^{-\frac{h}{pz}} \quad . \quad . \quad . \quad (18)$$

No formal proof of this formula has been obtained, but it is of the right form and gives the correct values for large values of x , and small values of f/pv . An additional check can be obtained by evaluating

$$\int_0^{\infty} C_0 dh = M/v.$$

This gives the value of C_0 due to an infinite vertical plane source emitting a mass M per unit area per unit time. At all points downwind of such a source, the value of C must be M/v , since no concentration gradients are present, and consequently there is no diffusion. This gives additional confirmation to equation 18. At great distances, then, the ground level concentration of dust from an infinite line source at any height above ground will fall off rather more rapidly than the inverse first power of the distance, the falling off being more rapid the larger the particles.

V. Diffusion from a Continuous Point Source.

If the source is concentrated at a point such as the top of a chimney, instead of being spread over an infinite line across wind, the lateral spreading must also be taken into account.

Here the duration of the sample time is of even more importance than in the case of vertical diffusion from a line source. If a really long sampling period be required, *e.g.* if it is desired to estimate the average atmospheric pollution during the whole year, then the governing factor will be the distribution of direction of the wind. The instantaneous width of the smoke cloud will be without effect in this case, since increase of width will decrease the average concentration in the cloud and increase the frequency with which the cloud overlaps any given point, the two effects exactly cancelling each other.

If the fraction of the year during which the wind direction falls within an arc θ be $a\theta$, and the mean wind velocity be v , then the average value of C for the whole year due to a chimney emitting a mass M of gas per unit time will be

$$\frac{Ma}{pvx^2} e^{-\frac{a}{v^2 x^2}} \quad . \quad . \quad . \quad . \quad . \quad (19)$$

The mean value of a will obviously be $\frac{1}{2\pi}$, and the variation of a with direction can be obtained from meteorological records, and is independent of any diffusion theory.

Equation 19 gives the value of C which is effective in all cumulative processes, such as the blackening of the neighbourhood by soot, and to a great extent the attack of structures by acid constituents of flue gas such as oxides of sulphur and nitrogen and HCl.

At points not far distant from a chimney, effects due to the maximum concentration over short periods may become of importance, *e.g.* the gases may be smelt, and in this case the effective sampling period can be taken as of the order of a few minutes to an hour, *i.e.* a period during which the mean wind direction is not likely to change appreciably.

In this case, at points which are situated at a distance from the chimney smaller than the velocity of the wind multiplied by the mean duration of the minor transitory changes of direction, the lateral spreading of the mean cloud will be governed by the swing of the wind and equation 19 will hold with a suitable value of a .

If σ be the standard deviation referred to a vertical plane through the mean axis of the cloud, then

$$\sigma \propto x.$$

Now

$$\frac{d\sigma}{dt} = \frac{D}{\sigma}.$$

$$\therefore \frac{d\sigma}{dx} = \frac{D}{v\sigma}.$$

If, therefore, $\sigma \propto x$, then $D \propto \sigma v \propto vx$. At distances such that σ is great compared to h , $\bar{z} \propto x$ and, as pointed out above, in these circumstances in the formula $D \propto vl$, it makes no difference whether l be identified with σ or \bar{z} . Again, therefore, at great distances $D \propto \sigma v$, so that σ/x is constant.

In the case of gas emission, the total mass of unit length of the cloud will be everywhere equal to M/v . The mass m over unit area of the earth's surface at a distance x downwind, and y to one side of the mean path of the cloud, must be a maximum when $y = 0$, and fall off to zero at values of y large compared to σ . If the diffusion coefficient be assumed to be a function of x or σ only, and independent of y , and if concentration gradients along the cloud be assumed small compared to those at right angles to its mean direction of motion, then

$$\frac{\partial m}{\partial x} = \frac{D}{v} \cdot \frac{\partial^2 m}{\partial y^2}.$$

These conditions are satisfied by the equation

$$m = \frac{M}{\sqrt{2\pi\sigma v}} e^{-\frac{y^2}{2\sigma^2}}. \quad (20)$$

If $D = qv\sigma$ then $\sigma = qx$.

$$\therefore m = \frac{M}{\sqrt{2\pi qvx}} e^{-\frac{y^2}{2q^2x^3}}. \quad (21)$$

Substituting this value of m for M in equation 12 gives for the ground level concentration due to a continuous point source,

$$C_0 = \frac{M}{\sqrt{2\pi p q v x^2}} e^{-\frac{h^2}{p^2 x} - \frac{y^2}{2q^2 x^3}}. \quad (22)$$

Similarly, for the case of dust with a free falling speed of f ,

$$C_0 = \frac{M \left(1.78 \frac{h}{p} \right)^{\frac{f}{p^2}}}{\sqrt{2\pi p q x}^{\frac{2}{p^2}} e^{-\frac{h^2}{p^2 x} - \frac{y^2}{2q^2 x^3}}}. \quad (23)$$

VI. Comparison with Experiment and Numerical Values of p and q .

The value of p can be estimated in various ways. Hellmann,⁵ from experiments over an open field at heights of from 2 to 32 metres, found that the wind velocity varied approximately as $s^{1/5}$. This is in general agreement with the observation that the velocity of a gas flowing in a

⁵ Met. Z., 1915.

pipe varies in the region of the pipe wall proportionally to the $1/7$ power of the distance from the wall. A later formula of Hellmann gives

$$v = a \log(z + b) - c,$$

where a , b and c are constants.

The mean of Hellmann's first formula and the pipe results gives $\frac{dv}{dz} \propto z^{-5/6}$, and Hellmann's second formula gives $\frac{dv}{dz} = \frac{a}{z+b}$. Now the product of the velocity gradient and the effective eddy viscosity must be constant and equal to the tangential force per unit area on the ground. Since the diffusion coefficient can be identified with the kinematic eddy viscosity, these two formulæ indicate that $D \propto z^{5/6}$ and $D \propto z + b$ respectively, agreeing reasonably well with the assumption made in this paper that $D \propto z$. An approximate estimate of p can be made from the first formula. It is known that above about 500 metres the wind velocity agrees well with the value calculated from the horizontal barometric pressure gradient. Also the tangential force per unit area on a plane for large scale phenomena tends to the limiting value of about $0.002 \rho V^2$, where V is the velocity at points remote from the plane. If then the velocity be assumed to vary as $z^{1/6}$ up to 500 metres, after which it becomes constant, then

$$\frac{dv}{dz} = \frac{V}{6(5 \times 10^4)^{1/6}} z^{-5/6},$$

$$\text{and} \quad 0.002 \rho V^2 = \rho D \frac{dv}{dz},$$

$$\therefore D = 0.073 V Z^{5/6}.$$

If v be the velocity of the wind at 100 metres, then the value of D at 100 metres is $0.02 v z$. This gives $p = 0.02$, a value which is probably too low, since the tangential force of $0.002 \rho V^2$ was obtained by experiments with smooth pipes and the tangential force on the earth's surface may well be considerably greater. If a cloud from a chimney be viewed from the side, then the opacity is probably a function of the total amount of matter in the line of sight. The apparent density will be equivalent to that from a line source, since lateral spreading is without effect on the opacity. The apparent greatest density at ground level then will occur when $px = h$, or at a distance $1/p$ chimney heights from the source.

Dobson,⁶ in a memorandum on atmospheric turbulence, gives a composite of eight successive photographs of a smoke cloud from a chimney. The maximum density at ground level is apparently about seven chimney heights from the source, giving $p = 0.14$. He states that on another day the apparent turbulence was 0.4 times as great, giving $p = 0.06$. In this case, there were a number of buildings immediately to leeward of the chimney, so that more turbulence would be expected than in Hellmann's case.

Experiments by Richardson⁷ on smoke clouds from small sources near the ground give a mean standard deviation in the vertical direction of 0.45 m. at a distance of 5 m. from a source 2 m. above ground. This leads to a value of p of 0.01, but these experiments again were carried out over a smooth field where the turbulence would be expected to be low.

⁶ Advisory Committee for Aeronautics, Reports and Memoranda No. 671, 1919.

⁷ *Phil. Trans.*, 1920, 221A, 1.

An average value of p is probably about 0.05, with possible variations by a factor of at least 3 in either direction. This value would make the apparent greatest density at ground level of the smoke cloud from a chimney occur at a distance of twenty chimney heights, whilst the actual maximum density, allowing for lateral diffusion, would occur at half this distance.

B. The Value of q .

Experiments by Richardson and Porter⁸ on the horizontal scatter of small balloons released nearly simultaneously and drifting distances of between 30 and 600 km. give a mean value of σ in the horizontal direction of 16 km. at a distance of 200 km. the best fit to their points being obtained if $\sigma \propto x^{0.9}$. This gives a mean value of q of 0.08 over this range of distances.

Now, the value of σ for horizontal diffusion is qx ; but for vertical diffusion from a source at ground level if $D = pv$, then $\sigma = \sqrt{2} px$. If, therefore, σ is the same in the horizontal and vertical directions, and the cross-section of a smoke cloud is roughly circular or semi-circular, according to whether it is formed at a great height or near the ground, then $q = \sqrt{2}p$. This indicates a value of p of 0.057 from the balloon results, in agreement with the mean value at short distances.

C. Sootfall in and near Towns.

It has been deduced above that the rate of deposition of dust at a distance x from a line source of intensity M is equal to

$$\frac{Mf}{pv} \cdot \frac{\left(1.78 \frac{h}{p}\right)^{\frac{f}{pv}}}{x^{1 + \frac{f}{pv}}} e^{-\frac{h}{px}},$$

where h is the height of the source above ground.

The D.S.I.R. Report on Atmospheric Pollution for 1931 gives an account of experiments which were carried out in the neighbourhood of Norwich. Norwich can be considered in this case as a line source of smoke about 2 miles in length. At distances between 2 and 10 miles from the centre of the city the rate of dust deposition at points immediately downwind varied as $A + B/x$, A being the rate of deposition of non-city dust. This agrees with the formula above if f/pv and h/px are both small. The value of f for a 20 micron diameter coal particle in air is 1.5 cm./sec., the mean value of v is about 500 cm./sec., and p can be taken as 0.05.

For particles of this size, $f/pv = 0.06$. The mean height of the chimneys of Norwich is probably about 15 metres, so that at a distance of 2 miles from the centre of the city, $e^{-h/px}$ will vary between 0.83 and 0.94. This difference from unity is partially compensated by the effect of the finite depth of the city, the mean value of $1/x$ being $\frac{1}{2} \log_e 3 = 0.55$, instead of 0.50 at a distance of 2 miles from the centre of the city. It would be expected, therefore, that the inverse first power law would hold with reasonable accuracy, as was found in practice.

It will be noticed that although there is a considerable range of values of p deducible from different sets of experiments, yet there is no apparent tendency for p to decrease as the scale of the experiments is

⁸ *Mem. Roy. Met. Soc.*, 1925, 1.

increased; in fact, the smallest values are deduced from the smallest scale experiments (Richardson). If n is appreciably less than unity in the expression $D = pvs^n$, then the value of p deduced on the assumption that $n = 1$ should fall off with distance from the source according to the law $px^{\frac{1-n}{2-n}} = \text{const.}$

This confirms the statement made above that effects due to the deviation of n from unity are unimportant compared to the variations of p with conditions of weather and surface.

VII. General Conclusions and Applications.

A theory has been developed by dimensional analysis for calculating the spreading of a smoke cloud from a chimney, and the results have been

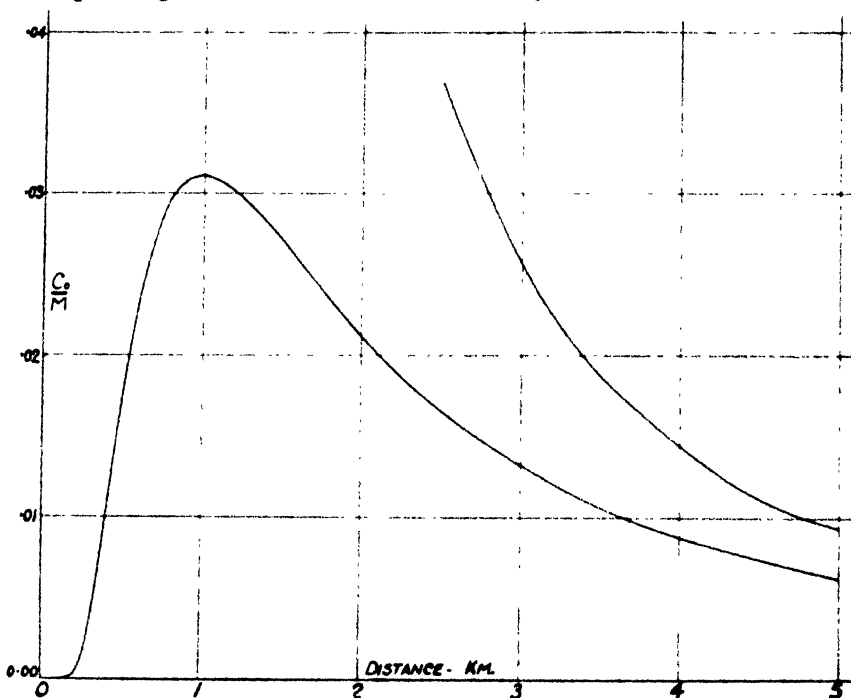


FIG. 1.

shown to agree reasonably well with experiment. At points close to the chimney the concentration at ground level is small, since but little smoke has diffused down to the ground. At a distance of the order of ten times the height of the chimney the smoke concentration at ground level reaches a maximum. The concentration at that maximum varies inversely as the square of the chimney height, and its actual value is almost independent of assumptions as to the variation of diffusion coefficient with height. At greater distances the concentration at ground level falls off again until after about fifty chimney heights the concentration varies as the inverse square of the distance and is independent of chimney height.

A formula is given for the concentration at all distances from the chimney foot.

Assuming that $p = 0.05$ and $q = 0.08$

$$C_g = \frac{100 M}{\pi x^2} e^{-\frac{20h}{x}} - \frac{78q^2}{x^2}.$$

The figure gives values of $\frac{C_0}{M}$ for various values of x for a chimney one hundred metres high, with a wind velocity of 5 m./sec. C_0 is in milligrammes per cubic metre, M is in metric tonnes per day, and the values are those for $y = 0$, i.e. at points on the ground directly under the axis of the cloud. The upper curve gives values of C_0 if $h = 0$, i.e. the difference between the two shows the effect of chimney height in reducing the atmospheric pollution at ground level. With a chimney 100 metres high the concentration is halved at 2.9 km., and at greater distances the effect of chimney height becomes progressively smaller. Over the range of distances covered by the curve the variation of dust concentration with distance is indistinguishable from that for gases, since the curves intersect at 3.56 km, and the slopes are very nearly the same for particles of the order of 20 microns diameter. This is not surprising, since in the absence of diffusion, coal particles 20 microns in diameter would not reach ground until they had drifted 33 km.

It may be pointed out that the general form of the curves is independent of any theory as to the variation of diffusion with height. In particular, the ratio of the yearly average contaminations produced by different types of source such as a power station and a town, at distances great compared to the chimney heights are independent of all theory. This point is stressed because this investigation was originally begun in order to find whether the superposition of the products of combustion of a power station in a town on those of domestic fires would cause an appreciable increase and in order to estimate the improvement attainable by using tall chimneys.

It is seen that although the improvement is great in the immediate locality, yet a mile or two away the effect of chimney height disappears completely.

GENERAL DISCUSSION.

Mr. F. I. G. Rawlins (*London*) said: It would be of great use to those who have to consider the influence of fogs and dust upon buildings and their contents if they could be provided with a three-dimensional scheme showing, not only the amount of material deposited at ground level at given distances from a chimney, but also the vertical distribution. Clearly, local conditions would influence the relationships enormously, but any method of obtaining a rough idea of the amount of deposit to be expected on the roof of a building of given height at a given distance from a chimney would be of considerable practical value. One imagines that fog and dust "shadows" are presumably cast by large obstacles, and this could be allowed for if some indication of vertical distribution could be obtained as a function of the other two variables.

Mr. G. Nonhebel (*Billingham*) said: It has been shown from the principles of eddy diffusion that the maximum ground concentration occurs at a distance of the order of ten chimney heights from the base of the chimney. A curve for one particular set of circumstances is given by Pearson and Bosanquet in Section VII. of their paper. For other circumstances, the maximum ground concentration C_0 in mgs./M² at the centre of the line of discharge will be roughly

$$C_0 = \frac{1.55 \times 10^3 M}{v h^2},$$

where M = mass rate of emission in tons/day, v = wind velocity in m./sec. h = chimney height in m. From this it may be deduced that when the wind-velocity is relatively low at 2 m./sec. and the emission is 60 tons SO₂/day, the maximum ground concentration with a chimney height of 330 ft. (100 m.) is 5 mgs. SO₂/M². (A diagram showing the progressive

increase in chimney height required to keep the ground concentration below 5 mgs./M³ has been recently published.)¹ This is not an unreasonable factor of safety, and yet few of the larger power stations fulfil this condition.

It is evident that further experimental observations are urgently required on diffusion of smoke from chimneys, and biological experiments on the toxic effects of SO₂ and SO₃ are similarly required. It would be of interest, also, to know how much of the SO₂ in an atmosphere is oxidised to SO₃ when it is dissolved in the moisture in the lungs.

Mr. C. H. Bosanquet (*Billingham*) said in reply: Measurements of numbers and size distributions of particles in the air at different distances from the source would be of great use in testing the theory. The size distribution should only vary very slowly with distance for particles less than 20 μ in diameter.

In reply to Rawlins: Small particles in the air will diffuse as a gas so that no true shadows can be produced by buildings. If a building is close enough to the source for an appreciable vertical concentration gradient to exist, then the downward currents behind the building are more likely to produce an increase than a decrease of concentration. Large particles will certainly be deposited preferentially on the windward face of a building, but diffusion close to the lee side will be abnormal due to the local disturbance of flow.

¹ Pearson, Nonhebel and Ulander, *J. Inst. Elec. Eng.*, 1935, 77, 1.

THE DISSIPATION OF FOG.

By PROFESSOR D. BRUNT, M.A.

Received 3rd April, 1936.

1. The Formation of Fog.

Fog is formed in air which is initially clear but damp, when the air is cooled to a temperature below its dew-point. The temperature of the air immediately above the surface of the earth is controlled by the temperature of the surface. The cooling necessary for the formation of fog may be produced in two ways; (a) by the loss of heat by long-wave radiation from the ground at night to a clear sky, or, (b) by the motion of warm damp air into a region where the surface of the earth is cold. Fogs formed by method (a) are known as "radiation fogs." Their formation requires a clear sky, and very light wind or calm. They do not form to the same extent on windy nights, as the turbulent mixing associated with strong winds distributes the loss of heat through so deep a layer that the dew-point is not attained.

Fogs of type (b) may form either over land or sea. At sea they form in such regions as the Great Banks of Newfoundland, where a warm damp current of air from the Gulf of Mexico flows over a sea surface cooled by the Labrador Current. Fogs form in precisely the same way over land, when, after a spell of cold weather during which the ground has become cold, a warm damp south-westerly current sets in. Such fogs may persist for days, with visibility limited to less than 100 metres. An example of such a fog occurred on Saturday, 15th February, 1936, persisting in places until the early morning of the 17th. After a week of fair and rather cold weather, a warm damp south-westerly current of air set in during the night of the 14th-15th.

2. Some Physical Facts.

Dense radiation fogs usually extend through a depth of 300 to 800 feet, while the temperature increases upward from the ground to the top of the fog by an amount which averages about 5° C. The amount of liquid water in a fog is from 3 to 8 per cent. of the amount of water present as vapour. Taking the mean value of about 5 per cent., we find that in a fog at 5° C. the amount of liquid water per cubic metre is 0.35 grammes.

Fogs formed by the motion of warm air over a cold surface have a mean motion of about 5 to 7 metres per second. True radiation fogs move so slowly that the usual meteorological instruments fail to record their motion. It is usually assumed that radiation fogs have a motion of the order of 1 metre per second, but accurate observations of this kind are lacking.

3. The Dissipation of Fogs.

For the sake of clarity we shall assume that the fog we have to dissipate is 100 metres deep, and moves at a rate of 1 metre per second, and that the clear space which it is desired to form shall be 100 metres wide, at least initially.

Any method of dissipating the fog which shall have any practical value must act rapidly through the whole depth of 100 metres, otherwise the cleared space will take the form of a tunnel sloping upward through the fog.

The methods of dissipating fog which have been put forward may be summarised under four heads, as follows :—

(a) The electrical method, which consists in subjecting the air to a very strong electrical field, preferably a brush discharge. There is no reason to suppose that this method could ever be effective in clearing such volumes of air as would be involved in any practical dissipation of fog.

(b) The mechanical method, which would bring down to the surface fog free air from above. The assumption that the removal of fog-laden air from the surface layers by suction would suffice to bring down from above clear air to replace it, does not appear justifiable, and the method has never been regarded a serious possibility.

(c) The thermal method of warming the fog until the fog-droplets are evaporated. This is considered in fuller detail below.

(d) The chemical method, which consists essentially in the removal of sufficient water vapour from the air which carries the fog droplets to ensure the subsequent evaporation of the droplets. This method is discussed more fully below.

4. The Thermal Method.

This method appears at first sight very promising, since the total amount of liquid water in a 100 metre cube is only 350 kilogrammes. To evaporate this will require about 2×10^8 gramme calories, or say 8 therms, which, if taken from the domestic gas supply, would only cost about five shillings. In practice, it would be impossible to warm the whole depth, without bringing the vertical temperature distribution to the adiabatic, with temperature decreasing with height at the rate of 1° C. per 100 metres. To produce this temperature distribution would require another 36 therms, making a total of say 44 therms. It thus appears that the expenditure of 44 therms would suffice to clear a space

100 metres \times 100 metres in a fog 100 metres deep. This space would slowly fill up again with fog as the result of the diffusion of foggy air laterally across the boundaries. If the fog had a general movement, the clear space would be carried away downwind, at the rate of 1 metre per second in the typical fog we specified above.

If the fog had a general motion of 1 metre per second, foggy air would cross the windward boundary of the space to be cleared at the rate of 10^4 (metre)³ per second. If this air were heated as it crossed the boundary, sufficiently to clear it of fog-droplets by evaporation, heat would have to be expended at the rate of 0.44 therms per second, say 27 therms per minute. The air cleared of fog would move downwind at the rate of 1 metre per second, and the effect would be to produce a clear space which would be 100 metres wide at the windward edge, becoming narrower as it proceeded downwind. I estimate that in a light wind the width of the clear space would be about 50 metres at a distance of 600 metres from the windward edge, at which the heat is applied. Computing the cost on the basis of the use of gas, we find that the cost of forming such a clear space and maintaining it clear for a further ten minutes would be about £35, which is small by comparison with the aircraft which might be saved by landing in such a space.

The difficulty of applying this method consists in the fact that it is not possible *a priori* to work out the best way of applying the heat to the foggy air. No individual element of air must be heated to a temperature very far above that of its immediate surroundings, otherwise its buoyancy will carry it up through the fog so rapidly that its excess of heat is merely wasted. The burning of gas at the rate of 5400 cubic feet per minute, over a front of 100 metres, is not the simple problem it appears at first sight.

It would be easier to produce the necessary amount of heat by burning petrol, methylated spirit, or some other liquid, in troughs suitably distributed. Experimental work would have to be done to determine the best distribution of the sources of heat. Dr. C. F. Brooks, an American meteorologist, has described in his book entitled *Why the Weather*, a successful attempt to burn a hole in a fog over an aerodrome by burning two 50 gallon barrels of petrol poured on the aerodrome. When the fire had died down there appeared a hole in the fog, through which an aeroplane which had been waiting for it was able to land.

5. The Chemical Method.

The formation of fog requires an atmosphere containing suitable nuclei on which condensation can take place. The appearance of the fog is preceded by a fall of temperature, and an increase in the relative humidity, until a stage is reached at which condensation takes place upon the nuclei. The precise value of the relative humidity at which condensation begins depends on the nature of the nuclei, being lower for very hygroscopic nuclei than for the less hygroscopic.

Recent work carried out by Bowes and Houghton at the Massachusetts Institute of Technology has aimed at dissipating fog by destroying the equilibrium between the fog particles and the surrounding medium. In this work, a very hygroscopic substance, calcium chloride, is introduced into the foggy air, with a view to reducing the relative humidity of the air in which the water droplets are suspended below the limit at which condensation could begin on the original nuclei. This destroys the

equilibrium between the fog particles and the medium in which they are suspended, with the result that the fog particles evaporate.

In a laboratory experiment an artificial fog was prepared, and sprayed with small drops of saturated solution of calcium chloride. The results of this trial were so promising that it was considered worth trying out the method in a large scale experiment. Full details are not available of the large scale experiment, but it appears that it was carried out on a sea fog, a type of fog which drifts inland from the sea, but does not as a rule penetrate far inland. The saturated solution of calcium chloride was sprayed over a front of 100 feet from horizontal pipes set 30 feet above the ground, so that the drops of the solution fell through the fog, and in so doing scoured the air of its water vapour. The clear air formed by the evaporation of the fog droplets was carried forward by the wind, and the result was that a lane of clear air appeared in the fog, 100 feet wide and extending about 2000 feet downward. The initial visibility in the fog was 300 feet.

Little more than these bare facts have been published, and few details are available as to the visibility before, during, and after the spraying. Such observations are indispensable if we are to form a clear idea of the extent to which the apparent clearing was really due to the spraying of solution of calcium chloride. We are definitely not in a position to say that the one trial which has been reported in the Press was carried out under typical conditions.

There are at least three aspects of the problem of the dissipation of fog by chemical means which deserve consideration. In the first place, the nature of the nuclei on which the fog droplets are originally formed is of fundamental importance, since their nature determines the relative humidity at which condensation will begin, and therefore also determines the relative humidity to which it is necessary to dessicate the air between the fog droplets in order to produce evaporation of the droplets. It has usually been supposed that in a city fog the nuclei are more numerous and more highly hygroscopic than in a country fog, and that therefore the city fog is a dense cloud of very fine drops in an atmosphere whose relative humidity may be well below saturation, while the country fog consists of larger drops suspended in a medium whose relative humidity is about 100 per cent. It therefore appears safe to assume that if the relative humidity in a country or sea fog could be reduced to 90 per cent., the drops should evaporate, and the fog disappear. In a city fog, however, it would be necessary to reduce the relative humidity of the air to a much lower figure than 90 per cent., possibly to 70 per cent., in order to produce complete evaporation of the fog droplets.

In the second place, the choice of the most suitable substance for spraying the foggy air has to be considered. For the purpose of experiments on feasibility of fog dissipation calcium chloride is effective, though it has considerable disadvantages as a final solution of the problem. Calcium chloride, on account of its acid properties, is a highly corrosive substance, and it can hardly be regarded as a suitable substance to distribute widely over an aerodrome, or any other locality where machinery of any kind is exposed.

In the third place there is the question of the amount of the spray to be used, and the method of distribution. The amount of calcium chloride in the dry state required to reduce the relative humidity of the air in a space formed by a 100 metre cube from 100 per cent. to 90 per cent. is 140 kilogrammes. Or if, as in § 4 above, we consider the fog to

move at the rate of 1 metre per second, and distribute the salt at the windward edge of the space to be cleared in such a way as to clear the air of its fog as it crossed this edge, it is found that the dry chloride must be sprayed at the rate of 84 kilogrammes per minute. Using saturated solution of calcium chloride instead of the dry salt, 300 kilogrammes of saturated solution of the salt must be sprayed per minute.

The most serious problem which arises in this method of fog dispersion is the mechanical one of the distribution of the hygroscopic agent. At first sight, anhydrous calcium chloride appears to have a great advantage in that it reduces the weight of substance to be sprayed to the lowest possible value. But on account of its hygroscopic quality the dry salt is difficult to store, and probably difficult to distribute without its clogging any apparatus used in the process. The saturated solution has the advantage that no very special precautions are necessary in storing it, but for its distribution in an effective way it is necessary to determine the optimum size of drop, and to evolve a jet capable of emitting drops uniformly of that size.

It appears to be unlikely that any method can be evolved for the dissipation of a fog in which there is no definite wind, since the dissipation would involve the distribution of the chemical agent (or of heat if the thermal method were used) over the whole of the area to be cleared. When the fog has a definite motion in a direction which is determinable, it is only necessary to distribute the chemical agent (or heat) along the windward edge of the space to be cleared. This is still a difficult problem to solve, but it should be possible to get some definite result by experiment even if the method of distribution fell short of perfection.

Brief descriptions of the work done in America in developing the chemical method of fog dissipation are given in the following papers:—

(1) "A method for the local dissipation of natural fog," by E. L. Bowles and H. G. Houghton (Jnr.), *Miscellanea of the American Philosophical Society*, 16th September, 1935.

(2) In *Technology Review*, October, 1934, p. 20, *et seq.*, is given a semi-popular account of the work done by Houghton on the scattering of radiation in fog, and on fog dissipation.

GENERAL DISCUSSION.

Mr. C. F. Goodeve (*London*) said: If this paper covers the present position of the practical dissipation of fogs, one is led to the conclusion that very little progress has been made. There seem to be many important questions still unanswered, only a few of which are indicated below.

In the calculation of the amount of gas required to evaporate the liquid droplets, no mention is made of the necessary temperature increase of the air. What effect on the cost would this have? The burning of gas or organic fuels produce water vapour and perhaps will do more harm than good? If a fog is dissipated, there is an increased loss of heat by radiation. Has any estimation of this loss been made? Have any calculations of the economic aspects of using calcium chloride been made? Could not fountains be used to avoid the erection of dangerous apparatus? Could the calcium chloride solution be cooled to increase its efficiency? If it were caught in a trough system, could not a cyclical process be operated? There are now standard methods for the economic control of humidity in factories by using refrigerating plant. Could not these methods be considered for the removal of fog?

Dr. R. Lessing (*London*) said that from experience with a coal cleaning process employing calcium chloride on a very large scale he could confirm that there was no danger of corrosion. He anticipated, however, that calcium chloride spraying on aerodromes would not be permissible as this electrolyte would coagulate the clay in the soil and inhibit the growth of grass, thus making the surface unsuitable for traffic on the ground.

Mr. W. Barrett (*Gerrard's Cross*) said: Heat could be applied to remove fog from aerodromes by buried networks supplied with low voltage current, as already done in horticulture. It seems also worth considering whether a cloud of drops of the order of 60μ radius could be laid down on the windward edge of the belt to be cleared, so as to bring down the fog particles. The cloud particles should be colder than the fog to avoid evaporation and subsequent condensation on fresh nuclei.

Dr. B. W. Bradford (*Billingham*) said: Attention may be drawn to work carried out in America on the dissipation of clouds by spraying with electrified sand from an aeroplane, in which excellent results were claimed. The economics of the method have not been investigated—it is probably expensive—but it might be applicable to special cases such as the dissipation of fog over estuaries, or of smoke screens or toxic smokes in warfare.

Dr. R. Meldau (*Berlin*) said: The idea of settling fog by dropping electrically-charged sand from aircraft has already been tried, but with the opposite effect.¹ Indeed, in this way Veraart brought about the formation of clouds and mists. Probably the Americans used one polarity and the Dutch the other; both made use of sands containing different size particles. Süring does not consider the Dutch method to be very hopeful. The experiments do not appear to have been followed up.

Dr. N. Fuchs (*Moscow*) (*communicated*): Experiments on rain-precipitation from the clouds by spraying calcium chloride on them from an airplane were recently made in U.S.S.R. For the most part, only structural changes in the clouds were observed after this operation, namely a clearing along the path of the airplane, the tearing of the cloud into several parts, etc. But in some cases a rainfall was actually obtained. At first the rain-drops were small, and their calcium chloride content high, but later on the drop-size increased and the rain was pure water.

Professor D. Brunt (*London*), in reply, said: My paper was not meant to be encyclopaedic, as Mr. Goodeve would appear to suppose. A number of points not mentioned in the paper, including those raised by Mr. Goodeve, were considered, and omitted from the paper as irrelevant to the main question. The necessary temperature increase of the air involved in the evaporation of the fog is allowed for in the estimate of heat required, and is shown in the first paragraph of section 4 of my paper to be $4\frac{1}{2}$ times the amount of heat required to evaporate the liquid water. The addition to the amount of water vapour present, involved in the use of liquid or gas fuel, is relatively small, and makes no essential difference to the estimates of cost which I gave. The increase in the loss of heat by radiation will not lead to any appreciable complication during an interval of time such as is aimed at in clearing fog. It has not been suggested that calcium chloride should be regarded at present as more than a suitable substance for experiments, and any calculations on the economic aspect of the choice of this particular compound appear a little previous. The suggestion of using fountains is quite impracticable. Drops of a size sufficiently small to present a reasonable amount of surface area to the air could not be sprayed up to heights such as are necessary for fog-clearing. The possibility of using a cyclical process such as Mr. Goodeve suggests might be considered at a later stage, but the first question is to decide whether the chemical method is at all feasible and effective. Methods involving the use of refrigerating plant, which may be effective in a closed vessel, or even inside a building, will not of necessity work in the open air.

¹ See A. Veraart, *Het kunstmatig verwekken van Regen*, N.V. Dr. Zuid-Holl. Boek-en Handelsdrukkerij, Gravenhage, 1930.

I now agree that I was mistaken in supposing that calcium chloride is corrosive, but this only removes one of several objections to the use of this substance.

Dr. Barrett's suggestion of using low voltage current to heat the air has never been tried, as far as I know. I cannot say how rapidly the heat from such a network would spread upward. A rapid diffusion of heat upward is not so necessary in horticulture, and the success of this method in horticulture does not of necessity mean that it would be effective in dissipating fog. Only an actual trial could determine the utility of the cloud of cold drops laid to windward of the area to be cleared.

The evidence as to the utility of electrified sand is so contradictory that it is impossible to assess its value.

The experiments described by Dr. Fuchs are puzzling, and it is far from obvious why the later stage of the experiments should give the precipitation of pure water.

VARIATIONS IN THE ATMOSPHERIC DUST CONTENT DUE TO MICRO-ATMOSPHERIC INFLUENCES.

BY ROBERT MELDAU (*Charlottenburg*).

Received 19th March, 1936, in German and translated by J. COLVIN.

Holmes and his co-workers, in a report ¹ by the American Committee of investigation on the smoke distribution from the Selby Copper Works in Montana (1915), first drew attention to the variable distribution of the smoke into regions. They marked "smoke routes" on a map (Table VI.) and established numerically that both the sulphurous acid content of the air and the arsenic and lead content of the soil were greatest at quite unexpected places in the region, namely, at 2.2 km. and 5.5 km. respectively from the chimney-stack. From the map, we may assume, without being able to particularise, that these phenomena are occasioned by a special configuration of the region, especially by locally restricted variations in the humidity (sea-shore, creeks).

If we insert numerically in the maps of the large towns, the measurements of the dust deposits, published by the Committee for Atmospheric Pollution, we find that the places of maximum deposition practically never coincide with the places of maximum industrial activity. The same conclusion is to be drawn both from the measurement of the annual dust deposit—as for example, in the town of Halle (Fig. 1)—and from the instantaneous measurements of Löbner in Leipzig ² in 1935.

Schaefererei Trotha is situated in a slightly built-up area, *Barbarastrasse* separated from the industrial centre. The dust centres in Leipzig are irregularly distributed away from the station and factories.

If we compare the very valuable map on the characteristics of the poisonous Meuse valley fogs ³ with a geographical map, we must again

¹ Bull. 98, U.S. Bureau of Mines.

² Alfred Löbner, *Horizontale u. vertikale Staubverteilung in einer Grossstadt*, Leipzig, 1935.

³ Batta, Firquet and Leqclerc, opposite p. 264 of their work.

conclude that it is not possible with any degree of certainty to explain, or even less to predict, where the zones of fog concentration must lie on geographical grounds and where fatalities are to be expected. Difficulties are encountered to a still greater extent if an attempt is made to explain why the fog concentration and the fatalities do not lie in the same zone, by assigning an essential part in precipitation to the land formation.

These and many other completely independent investigations, carried out moreover, for other purposes, seem to demand the following conclusions:—

(a) At certain places, the atmospheric pollution there arising is often disseminated irregularly into regions: wind direction and land formation do not always suffice to explain this irregularity.

(b) This irregularity is not merely a consequence of displacement of the smoke in bulk by the wind or of sedimentation during dispersal according to the size of particle, but is markedly variable.

(c) Thus fog and dust may first concentrate at unexpected places, sometimes quite remote from their place of origin.

The fine differences of temperature, humidity and of air currents (recently called microatmospheric) is an essential cause of this variation. Everyone who has carried out dust investigations has found that there exists not only in the open, but also in large factory rooms or assembly halls, a system of ascending and descending air currents and vortices, which, for example in closed halls, can bring about very stable zones of differentiated deposits.

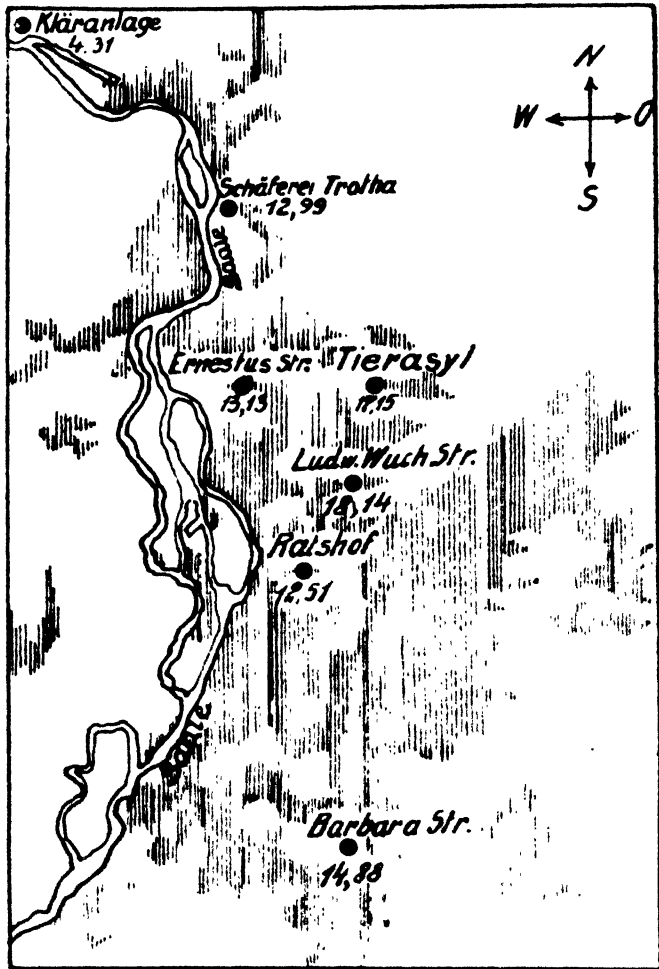


FIG. 1.—Dust deposit in Halle in 1931. (Relative values.)

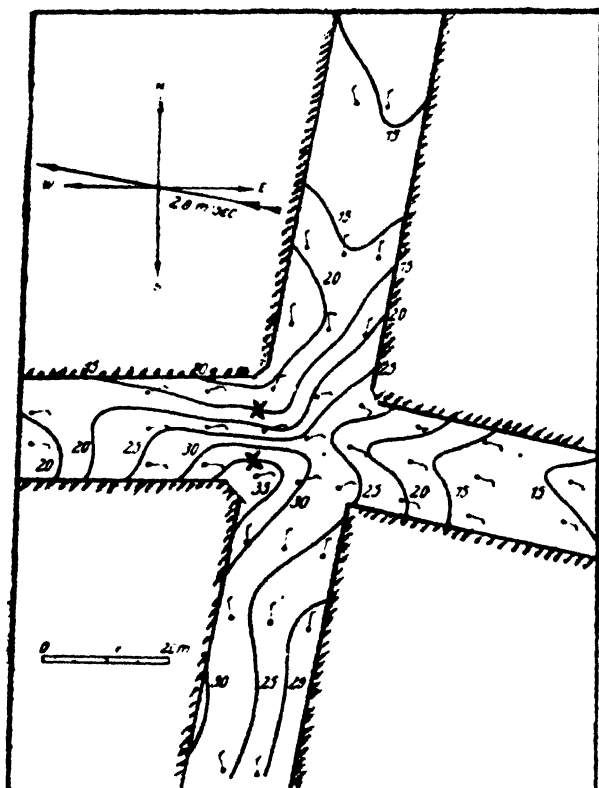


FIG. 2.—Dust distribution and wind directions at a street crossing in Leipzig (Löbner). (Dust content in 10^3 particles per litre of air.)

Above machinery the warm air ascends, divides on reaching the ceiling and sinks, to be cooled at the external walls or windows.

The following examples may serve to show how finely distributed these microatmospheric currents are, and what differences in dust content they may effect.

Fig. 2 (Löbner³) shows how the dust content is distributed at a street crossing by a wind velocity of 2.8 metres per second. At the points (marked with crosses) 10 metres apart, on the right- and left-hand sides of a street, the dust content fell from 35 to 15 particles, i.e., by more than 100 per cent., as a result of the slight change in angle of the direction of the street.

Fig. 3 shows the air currents and the temperatures mapped out for a Berlin street. The differences in the temperature and in the currents which contribute to the variability of the dust content

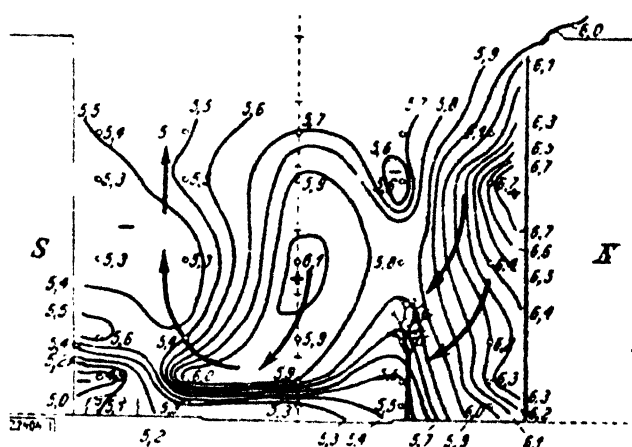


FIG. 3.—Air-current and temperature map in a Berlin street running east-west, under the influence of a south wind of 2.7 metres/sec.

content are clearly shown both at the ground and at higher levels.

³ Cp. J. Grunow, *Der Luftaustausch der Grosstadt*, Z. V.D.I., 1936, 80, 71.

GENERAL DISCUSSION.

Dr. R. Meldau (*Berlin*) (*communicated at the meeting*): It is worthy of note that, arising from the investigations upon which Firket has reported, the lines of equal dust content in open country do not coincide with the contour lines. I am indebted to Firket for showing me a diagram containing the measurements. It follows from the fact that such accretions and decrections of dust occur, that microanalysis of industrial dust should have exceptional significance, because it makes it possible to say whether a particular dust has originated from a particular source. As a result of extended experiments, I have demonstrated that such microanalysis can, in large measure, be utilised morphologically. The differentiation of the dusts may lie in their external shape, and surface condition, in their colour, reflectivity, or refractivity, or in their internal structure. These differences can readily be noted micrographically, especially if natural colours are used.¹ (The author then showed on the screen a small selection of his microphotographs.)

Mr. W. Barrett (*Gerrard's Cross*) said: Associated with wind, especially with gusty wind, are rapid variations of pressure. The air in a heap of dust responds to these and so the top particles are lifted into the system of eddies described by Dr. Meldau. It is probably for a reason of this nature that, under a falling barometer, dust is more readily lifted than at other times and this gives a physical explanation of the popular saying that blowing dust commonly foretells rain.

Dr. R. Lessing (*London*) called attention to the eddies produced in wind by buildings of even moderate height, and cited the case of an anemometer at a coastguard station on the Atlantic coast, the irregular working of which was traced to a cottage some distance away interfering with the streamline flow of the wind.

Dr. R. Meldau (*Berlin*), in reply, said: Settled dust is frequently lifted again. How settled dust may be lifted again from soil has been studied in the case of the sand-hills and of the ripple marks on sands, both in theory as in practice.

¹ See Meldau, *Archiv. Wärmewirtschaft*, 1930, 281; *ibid.*, 1931, 304; *Z.V.D.I.* 1931, 1467; 1935, 356; Stach, *Z.V.D.I.*, 1935, 513; Mohsch, *Pflanzenchemie und Pflanzenverwandtschaft*, Fischer, Jena, 1931.

THE ENERGY EFFICIENCY OF IONISATION IN ELECTRICAL PRECIPITATION.

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1. Introduction.

In the phenomenon of electrical precipitation of dusts and mists it is possible to distinguish at least three main processes which lead ultimately to the precipitation of the particles:

- (i) The ionisation of the gas in which the dust or mist particles are suspended.
- (ii) The transfer of electric charge to dust or mist particles in collisions between these particles and electrons, positive ions,

and negative ions; the ions concerned being those derived from the molecules of the carrier gas.

- (iii) The motion of charged dust or mist particles due to the electric field between the electrodes.

In this paper we shall be mainly concerned with process (i). We shall consider firstly the general character of the process of ionisation of the carrier gas, particularly in its relation to the Townsend coefficient of ionisation, the electric field, and the pressure of the carrier gas. After noting the main characteristics of the type of discharge used in electrostatic precipitation, we shall then consider how far the conditions in such discharges depart from the optimum for effecting the ionisation of the carrier gas.

2. The Townsend Coefficient of Ionisation.

It was shown by Townsend¹ that if a constant current of electrons, i_0 , be liberated from the surface of a (plane) metal electrode (for example, by allowing a beam of ultra-violet light to fall on it), and if a constant electric field be maintained between this electrode and some other plane electrode so that the electrons tend to move away from the surface at which they are liberated, then for any given pressure of gas in the space between the electrodes, the dependence of the total current flowing between the electrodes, i , and the distance between them, x cms., is given by

$$i = i_0 e^{\alpha x}, \quad (1)$$

where α is a constant. Townsend interpreted this exponential growth of the current with the distance between the electrodes by supposing that the electrons leaving the cathode acquire sufficient energy from their motion in the field to enable them to ionise the gas molecules in collisions, the electrons formed simultaneously with the ions performing similar collisions. He showed that α is a measure of the ability of the electrons to ionise, and is defined as the average number of ions generated (or of ionising collisions suffered) by an electron per cm. of its drift * motion in the direction of the uniform electric field between the electrodes; he termed α the coefficient of ionisation.

Numerous determinations, mainly by Townsend and his collaborators,² have shown that, in a given gas, αp^{-1} is a function of the ratio Xp^{-1} , where X is the strength of the uniform field between the electrodes, and p the gas pressure; by convention X is expressed in volts cm.⁻¹, and p in mm. Hg, so that Xp^{-1} is expressed in units of volts cm.⁻¹ mm. Hg.⁻¹. An important point concerning these experiments to determine αp^{-1} is that the current density was very small, being of the order of 10^8 electrons cm.⁻² sec.⁻¹ and that the pressure rarely exceeded 50 mm. Hg.

It is found that the dependence of αp^{-1} on Xp^{-1} can be expressed to a close approximation by the empirical† expression over a wide

¹ Townsend, *Electricity in Gases*, Oxford, 1915, Chap. VIII.

* The actual motion of the electrons is, of course, largely random; it is customary to speak of the component of the total motion in the direction of the electric field as the "drift" motion.

² Summarised in Knoll-Ollendorf-Rompe, *Gasentladungstabellen*, Leipzig, 1934.

† A theory of Townsend¹ which attempted to provide a theoretical basis for this expression is now recognised³ to be based on untenable hypotheses.

³ Cf., for example, Mierdel, *Handb. d. Experimental Physik*, vol. XIII., part 3.

range of Xp^{-1}

$$\alpha p^{-1} = k_1 e^{-k_2 p X^{-1}}, \quad (2)$$

where k_1 and k_2 are constants characteristic of the gas concerned.

A quantity related to α is the energy efficiency of ionisation, η ; this is defined as the average number of ions generated per electron-volt of energy supplied from some external source to maintain the discharge in which the ions are being produced. From the definition of α , it follows that the average energy gained by an electron from the field, X , whilst it produces α new ions, is simply X electron-volts, or

$$\eta = \alpha \cdot X^{-1} \quad (3)$$

Since

$$\alpha \cdot X^{-1} = (\alpha p^{-1}) \cdot (Xp^{-1})^{-1} \quad (4)$$

it follows that η is also a function of Xp^{-1} , and that values * of η may at once be computed by means of (4) from the published data for αp^{-1} and the corresponding values of Xp^{-1} . On substituting the approximate empirical expression for α in (3) we find that η will be approximately represented by

$$\eta = k_1 \cdot p X^{-1} \cdot e^{-k_2 p X^{-1}} \quad (5)$$

From this it follows that a single maximum, η_{\max} , is to be anticipated for η considered as a function of Xp^{-1} , and that this maximum value will be attained when

$$Xp^{-1} = k_2 \quad (6)$$

The data for η in air derived from the published data for αp^{-1} are shown in Fig. 1, from which it is seen that this quantity passes through a well-defined maximum, 1.45×10^{-2} ions per electron-volt for $Xp^{-1} = 400$.

Whilst little attention appears to have been paid previously ^{4, 5} to η or αX^{-1} , it must be pointed out that long ago Townsend ¹ recognised that the point of inflexion in the curves of αp^{-1} as a function of Xp^{-1} provided the explanation for the Stoletow effect, and, of course, the existence of such a point of inflexion is formally identical with a maximum in αX^{-1} . What does not appear to have been fully recognised until recently is that αX^{-1} (or as we shall refer to it henceforth, η) is an *energy efficiency* for the production of ions.†

Since η , the energy efficiency for the production of ions of the carrier gas, is clearly a matter of importance in any process of electrical precipitation, it is pertinent to enquire, firstly, how far this dependence of η on Xp^{-1} may be anticipated to remain valid in the corona discharges used in electrical precipitation, secondly, what are the values of Xp^{-1} in these discharges, and thirdly, how far the values of η for the usual corona conditions diverge from the maximum.

* The relation to convert η ions per electron-volt to practical units, A gms. of ions per K.W.H., is

$$A = 37.4 \cdot M \cdot \eta,$$

where M is the molecular weight of the ion concerned.

⁴ Townsend and McCallum, *Phil. Mag.*, 1934, 17, 678.

⁵ Cf., for example, *ibid.*, 1934, 17, 678.

† Von Engel and Steenbeck ^{6, 7} have discussed the importance of the related quantity $X\alpha^{-1}$, the average energy expended per ion produced.

⁶ Steenbeck, *Z. Physik*, 1929, 53, 192.

⁷ Von Engel and Steenbeck, *Elektrische Gasentladungen*, Berlin, 1932, p. 93.

3. The Dependence of η on Xp^{-1} in a Corona at Atmospheric Pressure.

It has already been mentioned that, in the experiments of the Townsend school to measure αp^{-1} , the current density was extremely low, and the pressures of the order of a tenth of an atmosphere, or less. The first important application of these data to other conditions was Townsend's prediction of the sparking potential between parallel plates in gases at the same range of relatively low pressures.⁸ The success attending this prediction indicates that the values of αp^{-1} are still valid for the current density *immediately preceding the breakdown*; whilst such current densities must be considerably greater than those in the

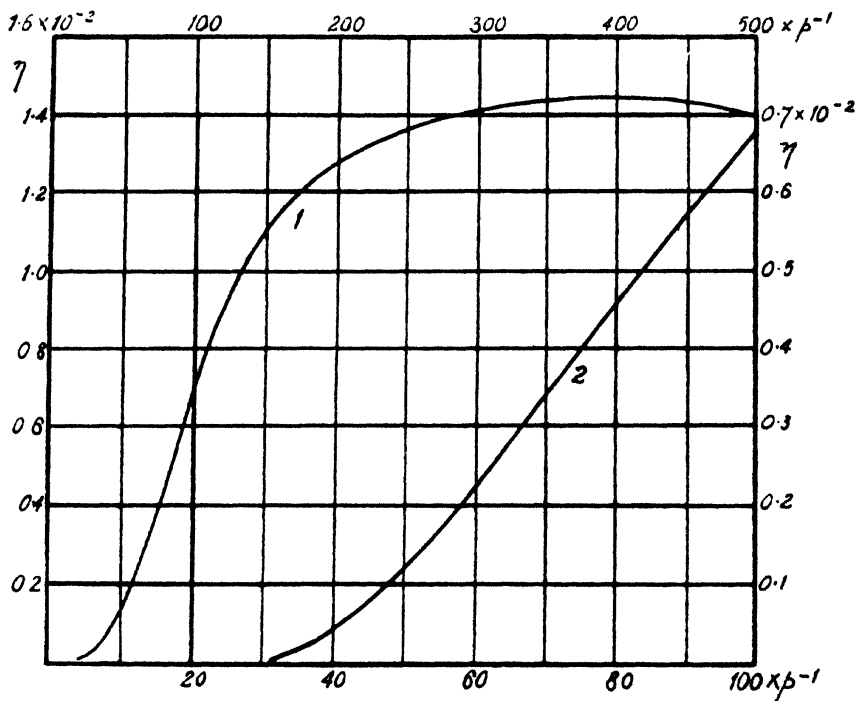


FIG. 1.—The energy efficiency of ionisation in air, η .
Curve 1, left hand and top scale; curve 2, right hand and bottom scale.

experiments to measure αp^{-1} , they must be less than those in a discharge maintained solely by the potential between the electrodes* (no measurements of the current density in the transition stage appear to have been made). In considering the experimental data for the sparking potential between parallel plates (and other shapes of conductors) at atmospheric pressure, Schumann,⁹ by using a simplified form of the Townsend condition for breakdown,⁸ came to the conclusion that the dependence of αp^{-1} on Xp^{-1} was no longer represented by (2). He proposed several

⁸ Townsend, *op. cit.*, Chap. IX.

* That is a "self-sustaining discharge"; in the experiments to measure αp^{-1} the current is maintained by the photo-electrons ejected at the cathode and by the interelectrode field.

⁹ Schumann, *Elektrische Durchbruchfeldstärke von Gasen*, Julius Springer, Berlin.

empirical formulæ, finally reaching the conclusion that the best of these was

$$\alpha = A \cdot X^{-2} \cdot \exp. (-B \cdot X^{-2}), \quad (7)$$

where A and B are positive constants, and X is the field strength * in kV. cm.⁻¹. Since the pressure is now constant (atmospheric) it does not appear in (7). Some idea of the empirical nature of this expression may be gained by noting that Schumann⁹ selects values of A and B for a particular electrode configuration. The corresponding value of the energy efficiency, which we will denote by η_s , then follows as

$$\eta_s = 10^{-3}\alpha \cdot X^{-1} = 10^{-3}A \cdot X^{-3} \cdot \exp. (-B \cdot X^{-2}). \quad (8)$$

It is interesting to note that η_s also passes through a maximum as X (and hence Xp^{-1} , since p is now constant) progressively increases; by differentiating (8) it can easily be shown that $\eta_{s, \max}$ occurs when $X = (2B/3)^{0.5}$, or

$$Xp^{-1} = (10^3/760)X. \quad (9)$$

The actual values of η_s cannot be computed from (8) because A is an unknown constant; we can, however, evaluate η_s/A which is proportional to η_s . By using Schumann's values for a wire-in-cylinder electrode configuration, $B = 6300$, it is found that $\eta_{s, \max}$ occurs at $X = 65$ kV. cm.⁻¹, or $Xp^{-1} = 85$. It is a little difficult to estimate the weight that Schumann himself attaches to the values of α given by (7), for, although he points out that these lead to a satisfactory (but empirical) interpretation of the phenomena of breakdown, he also points out that, for the above value of B , expression (7) predicts that α itself will pass through a maximum for $X = B^{0.5} = 79.5$ kV. cm.⁻¹, and of the existence of this maximum he expresses considerable doubt.

The next developments come from the Rogowsky school where Paavola¹⁰ showed that direct determinations of αp^{-1} in air at atmospheric pressure by a modified form of the Townsend¹ technique are in substantial agreement with the values predicted from (2), using values for the constants k_1 , k_2 derived from measurements of the Townsend school² at much lower pressures; these results were confirmed later by Masch.¹¹ It was then shown by Rogowsky that the use of these values of αp^{-1} in a modified theory of breakdown led to predictions of the actual conditions of breakdown in good agreement with experiment.¹² If Rogowsky's theory be accepted, then his results show that the values of αp^{-1} given by (2) are valid for atmospheric pressure and for current densities up to the value immediately preceding breakdown; again, although the absolute magnitude of this limiting current density is not known, it must be less than that in the discharge which follows. It then appears that Schumann's success in accounting for breakdown phenomena by using values of α given by (7) and a simplified form of Townsend's condition for breakdown must be attributed to mutually compensating errors; it follows that the values of η_s given by (8) are open to considerable suspicion.

In the absence of any other relevant further experimental data, it is necessary to glance at the theory of the Townsend coefficient α in

* On account of the high field encountered in discharges at atmospheric pressure, it is customary to express these in kV. cm.⁻¹, and for that we shall use the distinguishing symbol X where $X = 10^3x$.

¹⁰ Paavola, *Arch. f. Electrotech.*, 1932, 26, 443.

¹¹ Masch, *ibid.*, 1932, 26, 587.

¹² Rogowsky, *ibid.*, 1932, 36, 643.

order to attempt a prediction of the continued validity of the dependence of αp^{-1} on Xp^{-1} in the still greater current densities of an actual corona discharge.

4. The Theory of the Townsend Coefficient α .

Emeleus, Lunt, and Meek¹³ have recently shown that the theory of an electron swarm moving in a gas under the influence of a uniform electric field leads to the following expression for αp^{-1} :—

$$\alpha p^{-1} = W^{-1} \cdot k \cdot M(\bar{V}), \quad (10)$$

where W is the average electron drift velocity in the direction of X and is known as a function of Xp^{-1} from the work of Townsend and his collaborators,⁸ k a numerical constant $= 1.86 \times 10^8$, and

$$M(\bar{V}) = \int_0^\infty Q_i(V) \cdot V^{0.5} \cdot f(V) \cdot dV. \quad (11)$$

In (11) $f(V)dV$ is the energy distribution function for the electrons in the swarm and must be a function, $F(\bar{V})$, of the average electron energy, \bar{V} ; \bar{V} is known from the work of the Townsend school¹⁴ to be a function of Xp^{-1} for low current densities and gas pressures comparable to those used in the determination of αp^{-1} . The expression $Q_i(V)$, the probability cross-section for ionisation by an electron of energy V electron-volts, is the quantity determining the probable number of ionising collisions made by an electron of energy V per cm. of its (actual *) path through a gas. Since $f(V)dV = F(\bar{V}) = F_1(Xp^{-1})$ by experiment, and since $W = F_2(Xp^{-1})$ also by experiment, it follows from (10) and (11) that αp^{-1} is predicted by this theory also to be a function of Xp^{-1} .

By using the data of Townsend¹⁴ for the dependence of W and \bar{V} on Xp^{-1} , the data of Tate and Smith for $Q_i(V)$,¹⁵ and by making the assumption of a Maxwellian form † for $f(V)dV$, it is found that, for hydrogen and certain other molecular gases including air,‡ the values of αp^{-1} (and therefore also of η) calculated from (10) are in good agreement with experiment. This agreement between theory¹³ and experiment is evidence that the only assumption involved, that of a Maxwellian electron energy distribution, must represent§ very closely the actual distribution in the experiments in which αp^{-1} , W and \bar{V} were determined as functions of Xp^{-1} . But the theoretically calculated values of αp^{-1} are also in satisfactory agreement with the experimental values determined at atmospheric pressure,^{10, 11} for which there are no corresponding data for the dependence of W and \bar{V} on Xp^{-1} . At this pressure there are therefore three assumptions ¶ involved in calculating αp^{-1} from

¹³ Emeléus, Lunt and Meek, *forthcoming paper in Proc. Roy. Soc.*

¹⁴ Townsend, *The Motion of Electrons in Gases*, Oxford, 1925.

* The velocity W is the component of the actual velocity in the direction of the field X .

¹⁵ Tate and Smith, *Physic. Rev.*, 1932, **39**, 270.

† I.e., $f(V) \cdot dV = (27/2\pi)^{0.5} \cdot V^{0.5} \cdot e^{-1.5V/\bar{V}} \cdot dV$.

‡ Since there are no $Q_i(V)$ values for air, an approximate expression, based on that valid for other gases; this takes the form $Q_i(V) = A \cdot (V - V_0)$ where V_0 is now the "effective" ionisation potential⁸ of air, 16.3 volts.

§ Although the assumption of this distribution effects the correlation between experiment and theory, there is no proof that it constitutes a unique solution, although this is highly probable for other reasons.¹⁸

¶ It is now necessary to assume, in addition to the Maxwellian nature of the distribution function, that the dependence of W and \bar{V} on Xp^{-1} is the same as that measured at much lower pressures.

(10) and (11): whilst it is, of course, possible that the observed agreement with experiment may be due to mutually compensating errors, it is more reasonable to conclude that the dependence of W and \bar{V} on Xp^{-1} at atmospheric pressure is sensibly the same as that observed at lower pressures, and that the electron energy distribution is still Maxwellian. This conclusion relates necessarily to the relatively low current densities for which αp^{-1} was determined at atmospheric pressure.

It remains to consider whether this dependence of W and \bar{V} on Xp^{-1} and the distribution function may be anticipated to remain unchanged in the *considerably higher* current densities of corona discharges at atmospheric pressure. The early experiments of Wilson²⁸ indicate that the values of W in positive column discharges in air at low pressure are of the same order of magnitude as those determined for much lower current densities. Whilst there is no evidence for discharges at atmospheric pressure, a related case with which comparisons may be made is that of the formation at atmospheric pressure of ozone from oxygen in ozoniser discharges; this form of discharge is essentially a capacity limited corona. Lunt and Meek¹⁶ have calculated by expressions formally similar * to (10) and (11) the energy efficiency for the formation of ozone from oxygen as a function of Xp^{-1} in fair agreement with experiment. In performing these calculations it has been assumed, in addition to the existence of a Maxwellian electron energy distribution, that the dependence of W and \bar{V} on Xp^{-1} *for oxygen* at atmospheric pressure is the same as that measured¹⁴ at much lower pressures. Whilst this result might again be due to mutually compensating errors, it suggests strongly that the assumptions involved are correct. If this conclusion be accepted then it is reasonable to infer that it may also be anticipated that, also *in the case of air* in a discharge at atmospheric pressure, the electron energy distribution is sensibly Maxwellian, and the dependence of W and \bar{V} on Xp^{-1} is sensibly the same as that measured¹⁴ at much lower pressures. It then follows that the dependence of η on Xp^{-1} given in Fig. 1 may also be anticipated to remain valid in the conditions of atmospheric corona.

There is ample experimental evidence from probe data that, discharges at low pressure the electron energy is frequently Maxwellian,¹⁷ at least to a close approximation; and Druyvesteyn has recently pointed out in a theoretical investigation of the distribution function¹⁸ that, on account of the interaction between ions and electrons, the distribution for the high current densities of a self-maintained discharge (of which corona is one example) must approximate closely to the Maxwellian.

Summarising this discussion of the actual values of αp^{-1} and η at atmospheric pressure for low current densities, and their continued validity in a corona discharge, we see, firstly, that the direct determinations of Paavola¹⁰ and Masch¹¹ for low current densities indicate that no great reliance can be placed on the values given by the empirical expression of Schumann. Secondly, that although there is no direct evidence for the continued validity of these values in corona discharges, there are many lines of argument which indicate that this is probably the case.

¹⁶ Lunt and Meek, *unpublished work*.

* That is, expressions in which $Q_e(V)$ is replaced by the corresponding quantity for the excitation and subsequent dissociation of molecular oxygen by electron impact.

¹⁷ Compton and Langmuir, *Rev. Mod. Physics*, 1930, 2, 1; *ibid.*, 1931, 3, 192.

¹⁸ Druyvesteyn, *Physica*, 1936, 3, 65.

5. The Field in a Corona Discharge.

Whilst a complete theory of the mechanism of corona discharges is still lacking, it is generally accepted that ionisation by electron impact is confined to a luminous zone, the corona itself, close to one (or both in the case of a parallel wire system) electrode. It is therefore in this zone of the discharge that it is pertinent to the practice of electrical precipitation to consider the values of Xp^{-1} and the corresponding values of the energy efficiency for ionisation of the gas, η . For simplicity we shall confine our attention to the "wire-in-cylinder" type of electrode arrangement, and, in particular, consider the case closely related to current practice, a 1/16-inches diam. wire centrally placed with respect to a tube of 7 inch diam.; the radius of the wire, r , is then 0.080 cm., that of the cylinder, R , 8.9 cm., and the spacing between the electrodes, a , 8.82 cm. In order to illustrate certain theoretical predictions we shall also consider the case of a larger wire diameter, $r = 0.200$ mm., in the same sized outer cylinder so that the value of a is now 8.70 cm.

Unfortunately, there appear to have been no direct determinations of the field between concentric cylinders for continuous current corona discharges since those of Booth¹⁹ in 1917; and from the small scale diagrams reproduced in his paper it is impossible to estimate the field in the region of the actual corona, the diameter of which can be estimated from independent data. It is therefore necessary to approach the problem from the theoretical side, which, as has been mentioned, is far from being completely developed.

The earliest theory of the current-voltage relationship in corona discharges is due to Townsend.²⁰ In this it was assumed (amongst other things) that the field at the outer edge * of the corona, $X_{c,0}$, was equal to limiting critical field for breakdown at large electrode spacings between conductors of small curvature, about 30 kV. cm.⁻¹ in air at atmospheric pressure; it was also assumed that the ionisation in the corona was determined by the mean field in the corona which was itself assumed to be given by $0.5(X_c + 30)$, where X_c is the critical field at the surface of the wire necessary to produce corona. The assumption that $X_{c,0} = 30$ kV. cm.⁻¹ has also been used later by Peek²¹ in attempting to provide an explanation for the dependence of the corona diameter on the applied voltage. In a recent investigation Prinz²² has pointed out that the Townsend theory (together with several others) fails to predict the experimentally observed relationship between the applied potential and the power absorbed by the discharge, and that this failure is attributable, in part, to the neglect in these theories of the effects due to the field in the corona itself, and to the assumption that $X_{c,0} = 30$ kV. cm.⁻¹. Prinz then develops a modified theory of corona which takes account of the field in the corona; the great merit of this theory is that it predicts the observed potential-power relationship despite the fact that, as Prinz himself admits, it is to some extent empirical. Not merely does this theory enable calcula-

¹⁹ Booth, *Physic. Rev.*, 1917, 10, 266.

²⁰ Townsend, *op. cit.*, Chap. X.

* The symbol X will be used to denote field strengths expressed in kV. cm.⁻¹, thus distinguishing them from X which refers to volts⁻¹ cm.⁻¹.

²¹ Peek, *Dielectric Phenomena in High Voltage Engineering*, 2nd edition, New York, 1932.

²² Prinz, *Die Gleichspannungskorona*, Dr. Ing. thesis, München, 1934.

tions to be made of the field in the corona, \mathbf{X}_x , as a function of the radial distance x , but it also leads to the conclusion that $\mathbf{X}_{c,0}$ is less than 30 kV. cm.⁻¹ by an amount depending on the geometry of the electrode system. This latter conclusion is of particular importance for electrical precipitation, because, as may be seen from Fig. 1, the lower the value of \mathbf{X}_x (and therefore also of $X_x \cdot p^{-1}$) the lower is the value of η .

We shall now consider the application of Prinz's theory to the particular cases mentioned previously. The first relationship required is that of the dependence of the corona radius, x_0 , on the applied potential V kV. For this there are no completely satisfactory data, due mainly to the fact that this radius is difficult to define; we shall rely here on the photographic determinations with quartz lenses by Whitehead²³ who found that for values of V exceeding the critical value for the commencement of corona, V_c , by more than a small amount (of the order of 5 kV.) the relation is

$$x_0 = r + K \cdot (V - V_c), \quad (12)$$

where K is a constant depending on the geometry of the system. The case investigated by Whitehead approximating most closely to that we are now considering was for $r = 0.1165$ cm. and $R = 9.3$ cm.; from his data the value found for K is 0.035. Prinz adopts the value $K = 0.5$ cm. kV.⁻¹ which is obviously impossibly high, but from the data given in his Fig. 57 it appears that the value corresponding to the other conditions stated on that Fig. is $K = 0.0565$ cm. kV.⁻¹, but whether this is an experimental value is not clear. We shall adopt the experimental value $K = 0.035$, and consider the case for a relatively large corona radius $x_0 = 1$ cm. For the values of r and R selected, the values of V_c , found from the standard (experimental) expressions,^{21, 22} are approximately 25 kV. and 42 kV. respectively.

According to Prinz's theory,²² the field at the outer edge of the corona, $\mathbf{X}_{c,0}$, is given by

$$\mathbf{X}_{c,0} = x_0^{-1} V_c + (x_0 - r)/K \cdot \frac{\beta - 1}{\beta(\beta - 2)} \\ \times \left[1 - \sqrt{1 - \frac{\beta - 2}{(p-1)^2} \beta \left(\frac{1.32}{1 + \frac{x_0 - r}{KV_c}} - 0.32 \right)} \right] \quad (13)$$

where, for the case of concentric cylinders, $\beta = \log_e R/r$. After performing the calculations, it is found that for $r = 0.080$ and 0.200 mm. the values of $\mathbf{X}_{c,0}$ are, respectively, 2.3 and 7.3 kV. cm.⁻¹; the corresponding values for the potential across the electrodes according to (12) are $V = 50$ and 65 kV. respectively.

It must be pointed out that these values of $\mathbf{X}_{c,0}$ are surprisingly low, and until direct confirmatory evidence is available, we believe that they must be accepted with some caution. Since the wire electrode is negative, the corona itself may be regarded as a glow discharge in which, due to the high pressure, the negative zones have contracted to microscopic dimensions close to the wire, so that the main bulk of the corona will approximate to a positive column. There are unfortunately few data for positive column discharges in air, but Wilson²⁴

²³ Whitehead, *Proc. A.I.E.E.*, 1912, **31**, 839.

²⁴ Wilson, *Proc. Camb. Phil. Soc.*, 1902, **11**, 249, 391.

in 1902 showed that at low pressures, and for current densities comparable to those in corona at atmospheric pressure

$$Xp^{-1} = 35 \cdot p^{-0.5} \quad (14)$$

If we assume that this relation is still valid at atmospheric pressure, the value of Xp^{-1} is 1.28; this result would then signify that luminous discharges would be expected to occur in air at atmospheric pressure for this value of Xp^{-1} . It will be noticed that this value is considerably below the values of Xp^{-1} corresponding to the values of $\mathbf{X}_{e,0}$ derived from the application of Prinz's theory, the relation between Xp^{-1} and $\mathbf{X}_{e,0}$ being given by

$$Xp^{-1} = (10^3/760)\mathbf{X}_{e,0} \quad (15)$$

We may therefore find in these results of Wilson some provisional justification for accepting the low values of $\mathbf{X}_{e,0}$ predicted by Prinz's theory.

In order to calculate the energy efficiency of ionisation in the corona we require to know, firstly, the values of Xp^{-1} at the radial distance x ; these follow from (15) when $\mathbf{X}_{e,0}$ is replaced by the \mathbf{X}_x , the field at the radial distance x , which, from Prinz's theory, is given by

$$\mathbf{X}_x = x^{-1} \cdot x_0 \cdot \mathbf{X}_{e,0} \quad (16)$$

It is found that resulting values of Xp^{-1} inside the corona lie partly below the range in which αp^{-1} (and thence η) has been measured, $Xp^{-1} \geq 31$. For the values of $Xp^{-1} < 31$ the data of Masch do not suggest any obvious method of extrapolation; we have therefore made the somewhat arbitrary assumption that η has the constant value of $0.05 \cdot 10^{-2}$ corresponding to the measurements at $Xp^{-1} = 31$. Some justification for this procedure is afforded by the work of Emcléus, Lunt and Meek,¹³ who have concluded that at very low values of Xp^{-1} the electron energy distribution varies in such a way that the diminution of η as Xp^{-1} diminishes is not nearly so rapid as that predicted by (10) for a Maxwellian distribution. In any case, the error introduced probably leads to high rather than low values of η for Xp^{-1} less than 31. For higher values of Xp^{-1} , η has been derived from the data of Masch,¹² Fig. 1.

Since Xp^{-1} varies in the corona itself, the quantity of interest to evaluate is the average value of the energy efficiency of ionisation in the corona, $\bar{\eta}$. From the definition of η it follows that the rate of generation of ions at the radial distance x is given by the product of η and the rate at which energy is supplied to maintain the corona at this radial distance.

If I is the current in μA per cm. length of the wire-in-cylinder system, then the energy input to the corona per cm. length, P_c , is given by

$$P_c = 6.3 \cdot 10^{15} \cdot I \int_r^{x_0} \mathbf{X}_x \cdot dx \text{ electron-volts sec.}^{-1},$$

or, by (16),

$$\begin{aligned} P_c &= 6.3 \times 10^{15} \cdot I \cdot \mathbf{X}_{e,0} \cdot x_0 \int_r^{x_0} x^{-1} \cdot dx \\ &= 6.3 \times 10^{15} \cdot I \cdot \mathbf{X}_{e,0} \cdot \log_e x_0/r. \end{aligned} \quad (17)$$

Similarly, the total ionisation per cm. length, N_i ions sec.⁻¹, is given by

$$N_i = 6.3 \times 10^{15} \cdot x_0 \cdot I \cdot \mathbf{X}_{e,0} \int_r^{x_0} \eta_x \cdot x^{-1} \cdot dx, \quad (18)$$

where η_x is the value of η at the radial distance x . From these expressions the average value of η may be found, and is given by

$$\bar{\eta} = N_i \cdot P_c^{-1} = \frac{\int_r^{x_0} \eta_x x^{-1} dx}{\log_e (x_0/r^{-1})} \quad (19)$$

The values of the integral in (16) must be found by quadrature. After evaluating this integral and P_c for the two values of r under consideration, we find for $r = 0.080$ and 0.200 cm., respectively, $\bar{\eta} = 5.6 \times 10^{-5}$ and 1.22×10^{-4} . This shows that $\bar{\eta}$ is considerably higher for the thicker wire, but is still only 1.2 per cent. of the maximum value, 1.45×10^{-2} (Fig. 1).

It must, of course, be pointed out that this gain in the average value, $\bar{\eta}$, by using a thicker wire is achieved at the expense of a higher operating potential. It is therefore pertinent to consider next the overall energy efficiency, $\bar{\eta}_0$, referred to the total energy supplied to maintain the corona, P_t . Per cm. length of wire, P_t is given by

$$P_t = 6.3 \times 10^{15} IV \text{ electron-volts sec.}^{-1}.$$

Hence from (17) and (19) the overall energy efficiency of ionisation, $\bar{\eta}_0$, is given by

$$\bar{\eta}_0 = \bar{\eta} \cdot P_c \cdot P_t^{-1}; \quad (19)$$

the values of $\bar{\eta}_0$ derived from (19) for $r = 0.080$ and 0.200 cm. are, respectively, 6.55×10^{-6} and 2.20×10^{-5} . These results show that despite the increased operating voltage, there is still a considerable increase in overall energy efficiency of ionisation to be gained by using wire of larger diameter.

Summarising this application of Prinz's theory to the conditions of electrical precipitation, the most striking result is the prediction of very low values of the (ionising) field in the corona itself. The authors therefore believe that direct experimental determination of the field in corona would be of considerable importance, for the fact that Prinz's theory correctly predicts the dependence of the direct current corona loss on the voltage, and geometry of the system, cannot of itself be regarded as complete proof of the validity of this admittedly²² semi-empirical theory. The values of the average energy efficiency corresponding to these low corona fields are also extremely low compared with the predicted maximum; the calculations for central wires of different diameters indicates that a considerable gain of efficiency of ionisation may be achieved by the use of large central wires.

6. The Effect of Dust and Mist on η .

The calculations made in the preceding section relate to air alone; it is next necessary to enquire how far the conclusions reached there might be modified by the dust or mist present in actual precipitating conditions. In their recent summary, Mierdel and Seeliger²⁵ have pointed out that the presence of dust or mist lowers the critical corona voltage and increases the corona current for a given applied voltage. These results suggest that, other things being equal, the presence of dust or mist tends to lower the field in the corona and therefore also the energy efficiency of ionisation. As in the case of dust-free air discussed

²⁵ Mierdel and Seeliger, *Arch. f. Elektrotechnik*, 1935, **29**, 149.

in the previous section, no certain conclusions can be drawn until direct determinations of the field in the corona have been made when dust or mist is present.

Summary.

Reasons have been given for believing that the value of the energy efficiency of ionisation in air at atmospheric pressure determined at low current densities are valid in the higher current densities of corona discharges.

The recent theory of Prinz has been applied to calculate the field strength in corona for conditions approximating to those found in the practice of electrical precipitation. This theory predicts that the field strength will increase with the wire diameter.

From the values of the field strength derived from the application of Prinz's theory the overall energy efficiency of ionisation has been calculated. These are found to lie far below the maximum value.

This application of Prinz's theory has revealed that further experimental work is desirable to determine the dependence of corona size on the electrical and geometric factors, and to determine the field in the corona itself.

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THE PHYSICAL BASIS OF ELECTRICAL GAS PURIFICATION.

BY G. MIERDEL AND R. SEELIGER.

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It is well known that in principle electrical gas purification consists in subjecting the mixture of gas and dust to a unidirectional electric field in which an electric discharge in the form of a corona is taking place. The dust particles become charged in the latter, so that they move in the field towards one of the two electrodes where they are deposited for the most part as a firmly coherent layer. In principle, the charging and precipitation can take place in separate units, the gas stream flowing from one to the other, an arrangement which can be advantageous in many cases. In practice, however, almost without exception the two processes take place in the same apparatus, and this essentially takes one of two forms, wire-in-cylinder, or wire-and-plate.

(1) The Charging of Dust Particles in the Corona Discharge.

In gases at high pressure, which conditions alone are now relevant, it is possible to distinguish two zones in a corona discharge: there is a narrow, luminous zone in the neighbourhood of the wire electrode, the corona itself, and a completely non-luminous region which extends from the corona to the outer electrode. This visual difference between the two zones can be accounted for theoretically. In the corona there is a field distorted by space charge maintaining the discharge in a steady

state, and in which the necessary charged particles of the same sign as the wire are generated by electron collisions ("electron avalanche"). These charged particles are carried to the other electrode by the field in the non-luminous or "transport" zone. On account of the relatively small volume of the corona, the transport zone is practically the only region which is effective in charging the dust particles; a more exhaustive examination of the processes occurring in the corona is therefore only of secondary interest for the theory of charging the dust.¹

It will suffice to consider here a negatively charged wire, and therefore negatively charged carriers, in the transport zone, for these are the only conditions found in practice; that is why *ceteris paribus*, the current for negative corona is somewhat greater than for positive, and, more important still, the breakdown potential, which sets an upper limit to the operating electrode potential, is also appreciably greater for negative corona.² Under these conditions, negatively charged carriers (molecular ions) leave the corona and wander towards the anode, their motion being determined by their mobility and the field in the transport zone. The concentration of these carriers varies from case to case, and from place to place, depending on the field; for the usual conditions found in practice, an average value is 10^6 cm.^{-3} . The dust particles present thus exist in an atmosphere of (uncharged) gas, admixed with a negative ion gas, the latter having an extremely small partial pressure (about 10^{-11} mm. Hg). From this standpoint, the charging of the dust particles can at once be understood. The ion gas naturally takes part in the general thermal motion, and its temperature is but slightly higher than that of the (uncharged) gas. The dust particles suffer collisions with ions about 10^{11} times less frequently than with neutral molecules, and they must gradually become more and more strongly charged negatively, because the ions give up their charge on reaching the surface of a dust particle, and because there is no mechanism available by which the dust particles can acquire a compensating positive charge. This charging takes place with a gradually diminishing velocity because of the corresponding increase in the force exerted on an approaching ion. The finite time of transit of a dust particle through the ion atmosphere sets a limit to the charge which may be acquired, which, as experiment shows,³ is proportional to the radius, r , of the particles which are assumed to be spherical; for normal operating conditions the number of elementary charges, q , acquired by a dust particle, is given by $q = 2 \cdot 10^6 \cdot r$.

Apart from this purely kinetic treatment of the mechanism of charging, there is also the possibility that charging may occur in a region where there is a much higher field. In fact, such a field, under certain conditions, may be able to effect the further charging of a particle when the forces exerted by it on a colliding ion have become so large that, on account of its thermal motion alone, practically no further transfer of charge from ions is possible. The limiting charge, Q_s , which may be acquired by a particle under the influence of an external field, E , can be derived by considering the equilibrium between the forces at the surface of a particle, and the distortion of the (initially) homogeneous field by polarised dust particles, assumed spherical as before. If the dielectric constant of the particles is D , then Q_s in elementary units is given by

$$Q_s = e^{-1} [1 + 2(D - 1)/(D + 2)] E \cdot r^2,$$

where e is the electronic charge.

For the conditions obtaining in practice ($E = \text{about } 3 \text{ kV. cm.}^{-1}$), and for particles greater than about 1μ diameter, it can then be seen from the above expression that the limiting value of the charge which may be acquired under the influence of the field may exceed that arising from gas kinetic effects alone, *i.e.* that above this particle size the limiting charge increases as the square of the particle radius. This relationship has been frequently verified by experiment, for example, recently by Fuchs, Petrijanoff and Rotzeig.⁴

The question now remains as to whether the time of transit of a particle under the conditions obtaining in practice is adequate to allow the limiting charge to be acquired. Pauthenier and Moreau-Hanot⁵ have given the following expression for the growth of the charge with time:—

$$Q = Q_0(\pi \cdot b \cdot n \cdot e \cdot t)/(1 + \pi \cdot b \cdot n \cdot e \cdot t),$$

where b is the mobility of the ions ($b = 600 \text{ e.s.u.}$), n the carrier concentration (10^8 cm.^{-3}), and e the electronic charge. On inserting these values in the above expression, it is found that a transit time of 0.1 sec. is necessary for 90 per cent. of the limiting charge to be acquired. For a gas velocity of 2 m. sec.^{-1} , which is an average value for industrial practice, it is then seen that it would be necessary for the particle to traverse only 20 cm. in order to be charged; this distance is negligible compared with the several meters of effective precipitator length usually employed.

(2) The Drift and Precipitation of Dust Particles.

Having derived the charge on the dust particles, it is now possible to discuss the velocity with which they drift to the anode, or precipitation electrode. Assuming, as before, spherical particles, the drift velocity, w , for particles of present interest (*i.e.* from $0.1 - 10\mu$ diam.⁶) may be derived from Stokes' law, or

$$w = E \cdot e \cdot Q/(6\pi \cdot \eta \cdot r),$$

where η denotes the viscosity of the gas. The particles drift with this velocity w towards the anode where they remain and become precipitated. Although there is this loss of particles at the anode, the concentration of particles throughout the gas is maintained uniform by the turbulence of the streaming gas and also by the eddies due to the electric wind; it can then be seen that the concentration must fall exponentially along the gas stream through the precipitator. This exponential relationship between the concentration and the time of transit, or the length of the precipitator, was demonstrated by Anderson and Horne in America at the time when the technical development of electrical gas purification was beginning. More recently, Deutsch⁷ developed the complete expression relating the degree of purification ζ , defined as the ratio of the residual to initial dust content, to the drift velocity w , the mean gas velocity v , and the precipitator dimensions (length L , and electrode separation s). This expression takes the following forms:—

$$\begin{aligned} \text{for wire-in-cylinder systems } \zeta &= 1 - \exp. \{-2 \cdot w \cdot L/(s \cdot v)\}, \\ \text{for wire-and-plate systems } \zeta &= 1 - \exp. \{-w \cdot L/(s \cdot v)\}. \end{aligned}$$

It is thus possible to calculate the dimensions of a precipitator for a specified ζ from given data for the dust laden gas. Alternatively, the correctness of the above expressions can be tested, for example, from

measurements of the variation of ζ with v , and from these w could be derived and then compared with the theoretically calculated value.⁸

The field strength in a precipitator, E , is mainly determined by the space charge associated with the drift of unipolar carriers, and a knowledge of E is necessary to calculate w and Q . For a wire-in-cylinder system Townsend has derived an expression from which it follows that E is simply determined by the current density and b , except in regions in the immediate neighbourhood of the wire; this expression is $E = (2i/b)^{0.5}$ where i is the current per cm. of precipitator length. For the conditions obtaining in practice i may be taken as 0.01 ma. (or $3 \cdot 10^4$ e.s.u.) cm.⁻¹ and, using as before, $b = 600$ e.s.u., it is then found that $E = 10$ e.s.u., or 3000 volt cm.⁻¹. The derivation of E for a wire-and-plate system is beset with considerable difficulties, and it is necessary to assume that, to a first approximation, the values of E will not differ appreciably from those in a wire-in-cylinder system. On introducing these calculated values of E into the expressions given previously for the charging and the mobility, it may be shown that small particles of diameter less than 1μ drift with a velocity of a few cms. sec.⁻¹ practically independent of their diameter, and that, on the other hand, larger particles drift with a velocity proportional to their diameter, for example, about 25 cm. sec.⁻¹ for a diameter of 10μ .

The very good agreement between calculation and experiment affords evidence that there is no process contributing appreciably to the removal of dust in electrical precipitators other than those already mentioned. In particular, contrary to earlier opinion,⁹ the electric wind does not effect the directed transport of dust particles to the precipitation electrode, a conclusion that would be at variance with the continuity of the gas stream.¹⁰

(3) The Influence of Dust on the Electrical Conditions.

We will now turn to consider the effect of dust before and after precipitation on the electrical conditions in a precipitator; this is a matter of practical importance.

Uncharged dust has no effect on the corona discharge. The effect of charging the dust is to introduce a large number of carriers of greatly diminished mobility, and consequently a space charge. Whilst the fraction of the total current carried by the (charged) dust particles is little more than 1 per cent. under normal conditions, the space charge, being equivalent to the introduction of a negatively charged grid, has a considerable effect in diminishing the total current. It can be shown that the presence of this space charge necessitates a modification of the Townsend expression for the current-potential relationship in a wire-in-cylinder system, $i = V(V - V_c)$, in such a way that V_c is increased, the amount being numerically equal to the space charge per cm. length of the system;¹¹ an experimental verification of this deduction has been described by one of us.¹² In practice, the increase in V_c may amount to several kV., and leads to a diminution of the current, which latter effect may, however, be avoided by suitably increasing the electrode potential, V .

The effect on the discharge of the deposition on the anode of coherent layers of precipitated dust is much more complicated, and also introduces serious practical difficulties. The effect is mainly dependent on the structure and moisture content of the precipitated dust, and may,

therefore, take many forms. A systematic examination of the available technical data, together with laboratory experiments, has led at least to a qualitative elucidation of the principal phenomena.¹³ A characteristic effect is the appearance of ionisation on the precipitated dust layer: this can lead either to a stabilisation of the discharge, or to a disruptive discharge, sparking. In the former case, there is an increase in the current and a decrease in the efficiency of precipitation; in the latter case, the operating potential is diminished whenever spark-over due to the dust occurs, and consequently the efficiency of precipitation is also decreased.

The theoretical explanation of the foregoing effects arising from the precipitated dust layer on the anode may be expressed in the following terms. In the case of a layer of low ohmic conductivity, from dry dust, the potential across the layer due to the passage of the total current would amount to a considerable fraction of the electrode potential; the current therefore tends to flow through cracks in the dust layer in which ionisation of the gas has occurred. If the dust layer is sufficiently homogeneous for the cracks, and hence the alternative current paths, to be uniformly distributed throughout the layer, the stabilising effect previously mentioned is attained. On the other hand, if the current flow through the layer is highly localised, then the resulting high current densities at these points give rise to conditions favouring the development of sparking.

Various devices are employed in practice in order to minimise these difficulties. The resistivity of the (precipitated) dust may be very greatly diminished by the introduction of moisture, either before or after precipitation. Further, by suitable choice of the geometry of the precipitation electrode, the formation of thick layers can be avoided, the dust being collected through slits or holes ("pocket electrodes," "high power electrodes"). The wave form of the electrode potential has also an influence of behaviour of a precipitator. Whilst a d.c. potential is naturally most effective for a speedy charging of the dust (its maximum value being set by the breakdown potential for the system), it has been found sometimes to be advantageous to super-impose a 50-cycle wave on the usual d.c. potential; this is especially the case for dusts of low conductivity, and the effect is attributed to the possibility that this procedure affords for the "dust condenser" to discharge in the intervals of zero current, and thus avoid the building up of potentials which might otherwise lead to breakdown.

In conclusion, it may be remarked that the essential points of the theory of the physical processes involved in electrical precipitation are understood, and that further development will be concerned only with particular problems. Furthermore, the practical development of electrical precipitation has now been carried so far that serious difficulties may be anticipated in special cases only. The design of smaller and smaller units is, however, a field in which further development would be profitable. The production of these at an economic price, would be of importance to (national) hygiene, and the curve of development¹⁴ given at the Second World Power Conference in 1930 would then show a sudden increase.

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GENERAL DISCUSSION.*

Mr. A. G. Grant (Darlington) said: I would like to congratulate Meek and Lunt on their very interesting analysis of energy conditions inside the corona in a wire and tube discharge system. It would be interesting to know if in their work they have been able to throw any light on or draw any conclusions in regard to the conception of "minimum corona energy distance" evolved by Peek in the States, and to some extent accepted here. Peek's view is that in order that corona may occur, it is necessary that the gradient should exceed that necessary for breakdown for a certain minimum distance from the wire, this distance being vaguely connected with the minimum travel necessary for an ion to acquire ionising energy. It seems now that the very detailed analysis made by the authors ought to throw some light on this problem.

Dr. B. W. Bradford (Billingham) said: It is possible in practice to predict the performance of an electrostatic precipitator by the expression due to Deutsch.¹ For the case of the wire in cylinder arrangement, this takes the form:

$$\frac{n_0 - n}{n_0} = 1 - e^{-\frac{2kvt}{R^2 \cdot \ln R/r}}$$

Where n_0 and n are respectively the initial and final fume ion concentrations, k is the mean mobility of the fume ions, v is the applied voltage difference, t is the time of contact in the precipitator, R and r are respectively the radii of the outer and inner electrodes.

This formula is based on the simple assumptions:

- (a) that the combined effects of turbulence and ionic currents preserve a uniform ionic concentration across the cross-section of the tube,
- (b) that the field intensity can be expressed by the classical formula:—

$$X = \frac{1}{x} \cdot \frac{1}{\ln R/r}$$

No assumptions are involved regarding variation of intensity of ionisation in the corona with field intensity, or the average number of ionic charges acquired by fume ions.

There is no doubt that the Deutsch formula is capable of giving an accurate expression of the efficiencies of electrostatic precipitators. For example, by standardising conditions it can be used to determine the mobility of the fume ions in a homogeneous aerosol, and hence the particle

* On the two preceding papers.

¹ *Ann. Physik*, 1922, **68**, 335; *Z. techn. Physik.*, 1925, **6**, 423.

size, using the expressions derived by Rohman² or Ladenburg,³ for the relation between particle size and the number of charges on the fume ions. The method has been applied to H_2SO_4 mist, and has given excellent results.

It is suggested, therefore, that the factors discussed by the authors, while of fundamental importance in the theory of corona, are not limiting factors in electrostatic precipitators. It follows that no great increase in the efficiency of such precipitators can be expected by working under conditions of maximum energy efficiency of ionisation, whatever these may prove to be for the case of a corona discharge in a turbulent aerosol, which, as pointed out by the authors, are by no means identical with conditions in a particle-free gas.

Mr. A. G. Grant (*Darlington*) said: The Deutsch expression throws no light on the voltage-current characteristics of corona, and is to some extent an empirical value presupposing known corona conditions. Work of the type described by the authors is of fundamental importance as leading up to an exact knowledge of corona conditions and data for predicting them. In other words, it aims at elucidating corona discharge itself, rather than dust removal efficiencies in corona applications.

Dr. R. W. Lunt (*London*) said: (1) *In reply to Mr. Grant*, the authors have avoided any implications of Peek's "energy distance theory" by using experimental data for the corona diameter;

(2) *In reply to Dr. Bradford*: The authors desire to say that they agree with the views of Mr. Grant; the use of the term "efficiency of a precipitator" is a somewhat arbitrary and partial description of the performance of a precipitator if it is identified only with the fractional precipitation $(n_0 - n)/n_0$. The authors' paper refers to the energy efficiency of ionisation, and suggests by implication that this efficiency is one factor determining the energy efficiency of precipitation, η_D particles of dust or mist precipitated per unit of energy supplied. Clearly η_D is proportional to $(n_0 - n)/(I \cdot V)$ where I is the current through a precipitator maintained by an electrode potential V . The Deutsch expression for $(n_0 - n)$ is not in itself sufficient to predict the variation of η_D with V and r under otherwise constant conditions because it supplies no information on the corresponding variation of I with V and r .

It is, at least, a reasonable hypothesis that the rate of production of ions per unit of energy supplied will determine to some extent the rate of charging, and therefore also of precipitation, of aerosol particles per unit of energy supplied. It has been shown that there are reasons for believing that the energy efficiency for ion production may be increased above that for a standard precipitator by increasing V and diminishing r ; there is, therefore, reason to anticipate that such a variation of V and r will tend to increase η_D , and this is a result that cannot be inferred from a consideration of $(n_0 - n)/(I \cdot V)$ using the Deutsch expression for $(n_0 - n)$ alone.

² *Z. Physik*, 1923, **17**, 253.

³ *Ann. Physik*, 1930, **4**, 863; *ibid.*, 1932, **14**, 510.

A COMMERCIAL PLANT FOR REMOVAL OF SMOKE AND OXIDES OF SULPHUR FROM FLUE GASES.

BY G. NONHEBEL.

Received 2nd April, 1936.

Simultaneous removal of smoke, dust and acid constituents from flue gases by alkaline water in compact commercial plant has recently been achieved as a result of study of packings for absorptions towers. Such a plant is the Howden-I.C.I. grid packed gas washer, units of which were put into service at Swansea Power Station last year. Further units will shortly be in operation at the new Fulham Power Station. An account of this plant and process together with a survey of the problem of atmospheric pollution in large cities has already been given in *Applied Science Journals*.¹ The physical and chemical problems involved in the design of the plant are, however, of general interest.

Composition of Boiler Flue Gas.

For the specific case of boiler flue gas, the scrubbing plant may treat gas of composition :—

Grit and dust varying mostly from 5-100 microns	1-2 mgs./litre at N.T.P. for stoker firing. 5-15 mgs./litre for powdered fuel firing.
SO ₂	0.05-0.20 per cent. (= 1.3-5.2 mgs. SO ₂ /litre).
SO ₃	Traces ² up to 10 per cent. of the weight of SO ₂ .
HCl	Traces of the order of 0.1 mg. HCl/litre.
NO and NO ₂	Traces of the order of 0.1 mg./litre of combined nitrogen.
H ₂ O	Partial pressure of 0.05-0.08 atm.
CO ₂	10-16 per cent. by volume.
O ₂	9.3 per cent. by volume.

The temperature of the gas will lie between 110° C. and 150° C.

Description of Plant.

For a process for the removal of the stronger acids such as SO₂ from boiler flue gases to be generally applicable it is necessary to add alkali to the scrubbing water. The consumption of water by the process can then be minimised by recirculation of the wash liquor around the scrubbing towers. Lime or finely ground reactive chalk are the cheapest alkalis available and these are added in the form of a thin milk (5-10 per cent. solids).

Fig. 1 shows the principal items of equipment involved. The gas to be treated is brought by the flue 1 into a distribution chamber, which may be over 25 ft. long and of about 1 second's capacity and from which it flows laterally into scrubbing towers placed along the length of one or both its

¹ Pearson, Nonhebel and Ulander, "The Removal of Smoke and Acid Constituents from Flue Gases by a Non-Effluent Water Process," *J. Inst. Fuel*, 1935, 8, 119, and *J. Inst. Elec. Eng.*, 1935, 77, 1.

² H. F. Johnstone, "Corrosion of Power Plant Equipment by Flue Gases," *Univ. of Illinois Engineering Expt. Station Bulletin*, No. 228, June, 1931.

sides. These towers may be up to 12 ft. wide and are about 25-30 ft. high. Uniform gas distribution up through the towers is achieved by

primary elements 2, which consist of vertical wooden boards 3 ft. high and 3 ins. apart placed in echelon as shown in the diagram. These elements are fitted with $3\frac{1}{4}$ -in. wide pear section tops which collect the whole of the water falling from the packing above and distribute it as a film upon both sides of the elements. The speed of the gas up the empty tower is about 5 ft./sec. The primary elements are supported, however, in such a way that the gap between the pear section tops is only about 1 in so that there is an appreciable resistance to the flow of the gas which assists in the attainment of uniform distribution.

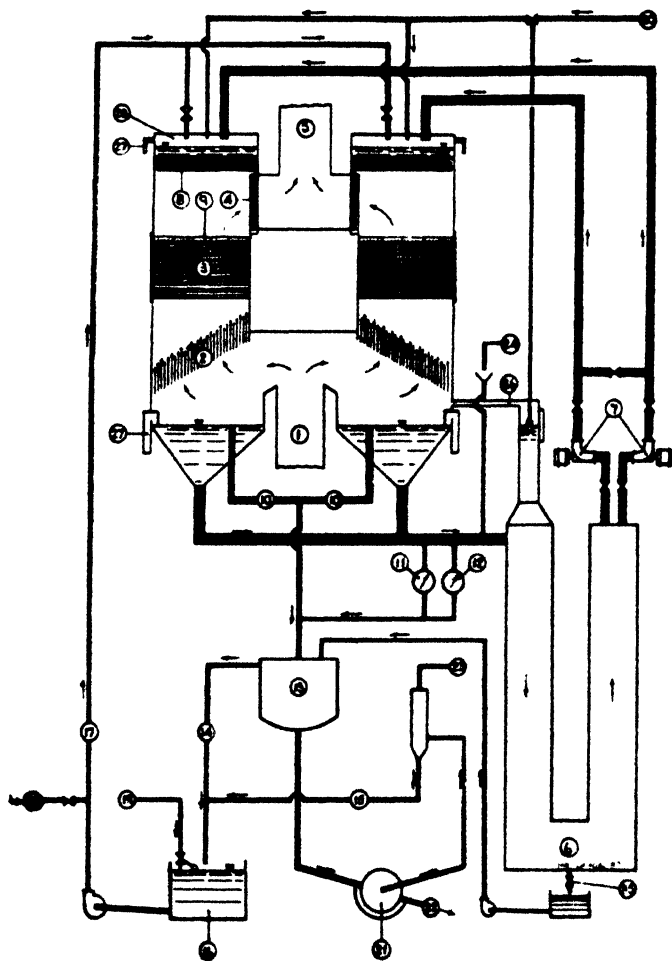


FIG. 1.

- | | |
|------------------------------------|--|
| 1. Gas inlet. | 15. Clarified liquor from filter. |
| 2. Primary elements. | 16. Mixed liquor tank. |
| 3. Grid packing. | 17. Mixed liquor return. |
| 4. Spray eliminators. | 18. To alkali preparation plant. |
| 5. Gas outlet. | 19. Make up water supply. |
| 6. Delay tank. | 20. Emergency make up water supply. |
| 7. Recirculation pumps. | 21. Rotary vacuum filter. |
| 8. Liquor distributors. | 22. Dewatered solids (rejected from system). |
| 9. Film feeders. | 23. To vacuum pump. |
| 10. Purge. | 24. Alkali supply and control. |
| 11. p_H recorder. | 25. Delay tank sludge cock. |
| 12. Solids recorder. | 26. Pressure equalising pipe. |
| 13. Settler. | 27. Emergency overflows. |
| 14. Clarified liquor from settler. | 28. Liquor head tank. |

Diagrammatic arrangement of Howden I.C.I. Flue Gas Scrubber system.

obtained from a cement kiln. The final scrubbing is effected by a height

Most of the coarse dust, namely, about half of the total dust, and about half of the SO_2 in boiler flue gas, are removed by the water passing over the primary elements. This section of the plant can withstand dust loadings of even 30 mgs./litre such as may be

of only 3 ft. 6 ins. of a special open grid type of packing 3. The grids found most effective for this duty, as determined by high efficiency and low resistance, are composed of thin wooden laths 1 inch deep, $\frac{3}{32}$ inch thick, held vertically $\frac{1}{2}$ inch apart by thin brass or wooden "carriers." The grids are piled on top of each other, the laths of one grid being at right angles to those immediately above and below. The grids are usually built for ease of handling in blocks four sections deep and 4-6 ft. square. The "carriers" are 12-15 ins. apart and are staggered so as to avoid division of the pile of grids into a number of small cells.

The gas rises through the grids and passes out through one or both of the long sides of the towers through spray eliminators 4. These consist of boards about 4 ft. high, 4 ins. wide, $\frac{1}{2}$ inch thick, and $1\frac{1}{2}$ -2 ins. apart arranged in a double V or zigzag formation. The height of these boards is chosen so that the velocity of the gas out of the tower does not exceed 6 ft./sec. From the spray eliminators the gas is led along flues to the boiler induced draught fan and delivered to the chimney.

Owing to the large volume of water required to wet the packing and to prevent scale formation thereon (see below), economy in washing water is achieved by recirculation of the used liquor around the scrubbing towers. The main liquor flow is shown by the heavy lines in the diagram. From the pumps 7 the liquor is fed to the head tanks 28, through pipes set at such an angle that the swirl produced is sufficient to prevent settlement of the dust, etc., in suspension. In the base of the head tanks are holes $\frac{1}{2}$ inch diameter, and about 9 ins. apart through which the water flows on to a 9-inch depth of liquor distributing grids 8. The latter consist of wood bars, $\frac{1}{2}$ inch square in cross-section and spaced $\frac{1}{2}$ inch apart, which serve to distribute the water from the nozzles as a fine rain on to the packing.

For efficient utilisation of the scrubbing fluid, it is important that it should flow as a film on the surface of the scrubbing packing. This is because the absorptive capacity of a simple spray is relatively low, since the relative turbulence between gas and liquid is low. The turbulence of the gas as it passes through the grid packing is, on the other hand, appreciable, and is sufficient to throw the humidified dust particles on to the liquor film, which then retains them. Moreover, the liquid is thoroughly mixed as it flows from each layer of laths to the layer at right angles below, and this mixing ensures that there shall be no appreciable concentration of dissolved SO_2 at the surface of the film which will reduce the absorption rate.

The rain of liquid is therefore fed as a film on to the grids by means of a number of laths 9, set at an angle like a horizontal venetian blind. These film feeders ensure that no free liquid falls through the $\frac{1}{2}$ -inch square lattice of the grids.

The normal liquor recirculation rate which is required in order to give a sufficiently thick film on the grids to prevent ash deposition upon their surface is 7 litres/hour per cm. periphery of each grid or about 7000 litres/hour per square foot of cross-section of the grid. This gives a film thickness of 0.9 mm.

From the grids and primary elements, the liquid passes through a shallow hopper into a large capacity "delay" tank 6, from which it is pumped back to the scrubbing towers by the pumps 7.

Due to the use of a closed liquor system the water in circulation is saturated with respect to calcium sulphite and calcium sulphate, and can, under certain circumstances, become appreciably supersaturated. One of the principal problems involved in the design of the plant is the control of this supersaturation in order to prevent deposition of scale on the scrubbing surfaces which would choke the tower.

Supersaturated solutions of CaSO_3 and CaSO_4 are relatively stable even in contact with crystals of their solid phase, and about 3 minutes in each case are required for a reduction in supersaturation from 5 mg.

equivs./litre to 2 mg. equivs./litre above normal saturation in presence of over 3 per cent. by weight of their crystals. Fortunately supersaturated solutions of these salts do not begin to deposit crystals spontaneously on clean wood (free from crystals) until the level of supersaturation is somewhat over 5 mg. equivs./litre. Consequently the plant is designed so that the liquor is proportioned to the gas rate, its sulphur loading and the degree of oxidation occurring in order to keep the amount of CaSO_3 and CaSO_4 formed in each liquor recirculation below 3 mg. equivs./litre. The extent of oxidation which occurs when SO_2 is absorbed by this solution of calcium bicarbonate is only slightly affected by the oxygen content of the flue gas and is mainly dependent on the oxidation catalysts (Mn, etc.) derived from the lime and the ash and possibly by the small traces of oxides of nitrogen absorbed. With a plant on full load the proportion of total absorbed sulphur appearing as CaSO_4 varies from 30-50 per cent. with stoker fired boilers to 50-80 per cent. with powdered fuel boilers.

When the sulphur content of the flue gas is less than 3 mgs. SO_2 /litre, the controlling factor in the size of the scrubbing towers is the maximum gas flow that can be passed through the grids without stripping off the liquor film.

From the last paragraph but one it follows that it is necessary to allow at least 3 per cent. of calcium sulphite and sulphate crystals to accumulate in the liquor and to allow time for crystallisation before pumping the liquor back to the scrubber if building up of supersaturation and consequent scale formation are to be avoided. In plants where the scrubbing towers are in an elevated position, the delay tank can conveniently take the form of a U tube supported on the ground as shown in the diagram. The diameter of the rising leg of the tube is chosen so as to prevent settlement of the suspended solids.

Accumulation of suspended solids above a predetermined level is prevented by purging a small flow of the liquor to a settler 13 or a rotary filter 21, where the solids are removed as a mud containing 30-50 per cent. of water. The clear liquor plus water required to make up losses in the mud and by evaporation is returned through the tank 16, and the pipe 17, to the head tank, where it reduces the supersaturation of the entering circulating liquor.

The quantity of purge is set by reference to an instrument 12, which indicates the specific gravity of the slurry. In one form of indicator this takes the form of a compressed air depth gauge used with a constant depth of flowing slurry.

Alkali Control.

The milk of lime or chalk for neutralisation of the absorbed SO_2 is added continuously at 24, just before the delay tank. The increase in p_H at this point reduces the solubility of CaSO_3 appreciably and assists rapid crystallisation of this compound.

For efficient SO_2 removal, and also in order to prevent corrosion of the steel towers and pipes it is necessary to control the p_H of the circulating liquor fairly closely at 6.3 ± 0.2 at the base of the scrubber. Addition of excess alkali is wasteful, as it is lost as CaCO_3 in the purge liquor. With control at p_H 6.3, the p_H after the delay tank seldom rises above 6.8, and since the liquor is saturated with CO_2 , both lime and chalk are almost completely dissolved as $\text{Ca}(\text{HCO}_3)_2$, and this is the effective scrubbing agent. The alkali loss is not more than 10 per cent.

The p_H is measured by passing a small flow of hopper liquor to a cell 11, containing a glass electrode-calomel combination. The E.M.F. is measured on a Cambridge thermionic valve potentiometer worked off the power mains and the reading is recorded on a chart. Suitable relays can be fitted to the instrument to enable it to control the lime addition valve automatically.

It is found that the solutions render the glass electrodes sluggish and inactive after 5-10 days' service, but they can be readily cleaned with 5 per cent. HNO_3 .

Moisture Content of Scrubbed Gases.—Since the grid scrubber is a highly efficient mass transfer apparatus the gas leaving the plant is saturated with water vapour and is cooled to the wet bulb temperature of the inlet gas. The circulating liquor is at the same temperature.

As the issuing gas is substantially free from SO_2 and SO_3 , which might stabilise a mist cloud, the plume of steamy vapour which issues from the chimney rapidly dissipates and becomes invisible.

Draught Loss.—Owing to the open nature of the scrubber grids, the draught loss across the whole plant including flues is less than 1 inch water gauge.

Smoke from Cement Kilns.—The pilot plant has also been fully tested on gases from a cement kiln. In these experiments the amount of alkaline dust collected by the liquor from the gases was sufficient to neutralise all the SO_2 . The calcium sulphite served also to absorb most of the H_2S in the gas.

Pilot Plant.—Fig. 2 is an isometric view of the complete Pilot Plant at the Billingham works of Imperial Chemical Industries Limited, where the design details of the process were worked out. The various items of the plant can be clearly seen. The scrubbing tower was 4 ft. square.

Plant Efficiencies.—The table shows some of the efficiency figures that have been obtained with the Pilot Plant on full load, and also at the powdered fuel power station at Swansea.

Plant.	Substance Measured.	Concentration. Mgs. litre at N.T.P.		Per Cent. Elimination.
		Inlet.	Exit.	
Pilot	Dust from cement kiln	10.4	0.12	98.8
		31.9	0.35	98.9
	Dust from powdered fuel boiler	9.6	0.26	97.2
		11.8	0.21	98.2
Swansea	" " "	—	0.41	{ over 98
			0.32	
Pilot	SO_2 and SO_3 measured as total sulphur	1.87	0.0033	99.8
		1.76	0.0632	96.4
Swansea	SO_2 and SO_3 measured as total sulphur	0.642	0.0018	99.7
		0.834	0.0020	99.7
Pilot	HCl	0.190	0.0061	96.4
"	Oxides of nitrogen as nitrogen	0.171	0.060	65
		0.246	0.091	63

The high efficiency of the plant for dust removal has also been amply shown by the ease with which it removed black smoke from a pulverised coal boiler when combustion conditions are deliberately made bad. The figures show, too, that the high efficiencies predicted from the Pilot plant experiments have been fully confirmed on full size commercial units.

The author's thanks are due to Dr. Lessing for results of laboratory experiments on rates of desupersaturation of calcium sulphate solutions; to the Swansea Corporation and their Consulting Engineers, Messrs. Preece, Cardew and Rider, for permission to publish preliminary figures for Swansea Power Station; and to the directors of I.C.I. (Fertilizer and Synthetic Products) Ltd., and of J. Howden & Co. for permission to publish this paper.

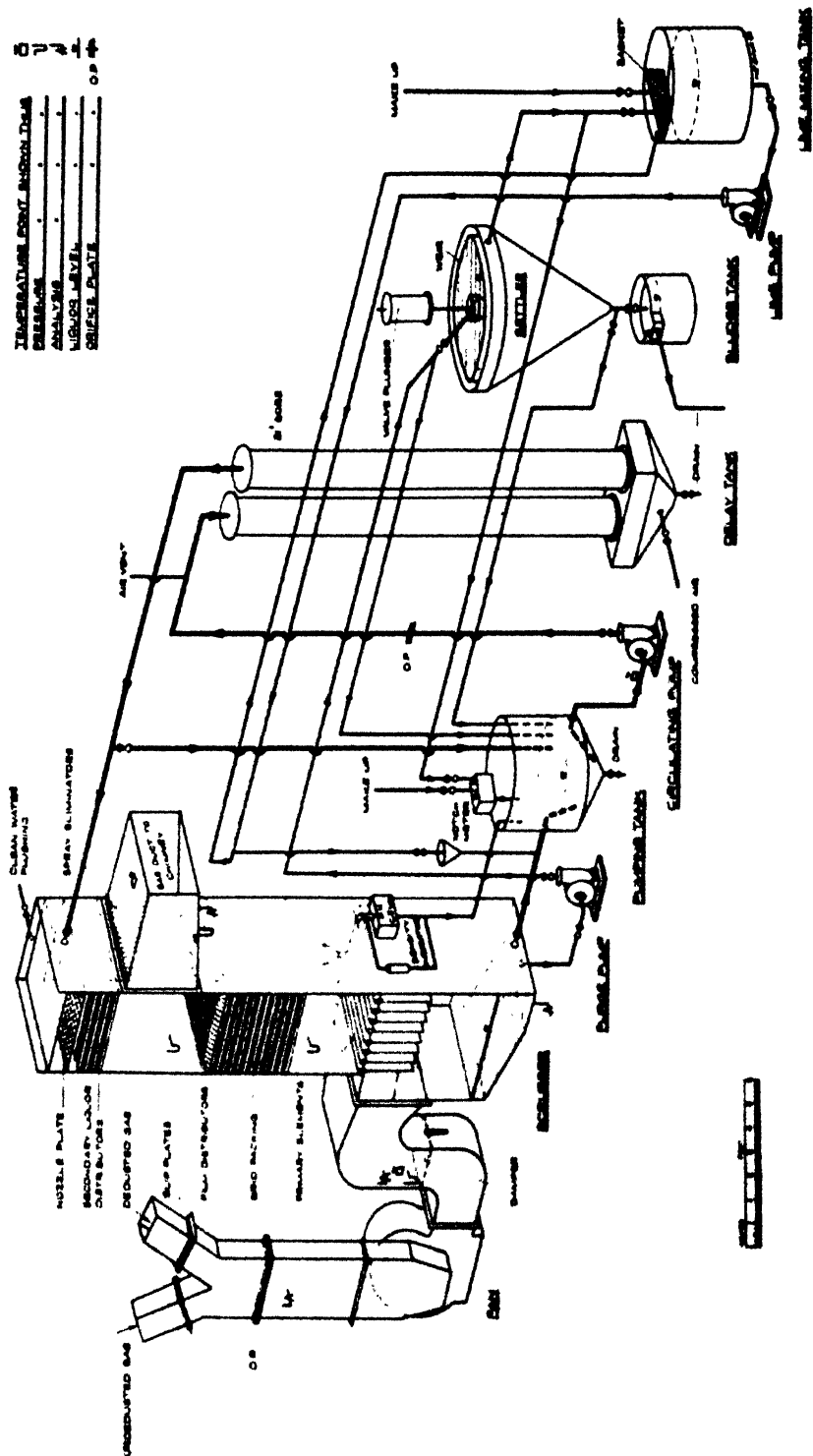


FIG. 2.
Layout of Billingham Experimental Plant.

GENERAL DISCUSSION.

Mr. W. A. Damon (*London*) said : As far as I am aware, there are only two plants where efficient removal of acidity from flue gases is practised. One is at Battersea Power Station, where the plant is remarkably efficient. Great credit is due to the London Power Co. for their efforts in this direction, but the Battersea scheme is not of very wide applicability in that it requires for its operation large volumes of naturally alkaline water, such as are available from the Thames. The Howden-I.C.I. plant described by Nonhebel is free from this disability, the only water required being that to make up loss by evaporation. In the event of ample alkaline water being available, can the scrubber operate without recirculation or is it necessary that the scrubbing liquor should have such an alkalinity that recirculation is necessary in the interests of economy?

One would like to see a much wider application of flue gas washing. Dr. Pearson demonstrated in a paper before the Institute of Fuel¹ that the loss to the country occasioned by sulphur oxides in the atmosphere amounted to 10/- per ton of coal burned, and that it was, therefore, an economy to spend anything less than that sum on flue gas washing. The manufacturer, however, does not regard the matter quite in that light. Can Mr. Nonhebel tell us whether he can see any possibility of economy in the operation of the plant by making any use of the calcium sulphate mud which is produced.

Dr. R. Lessing (*London*) said that the successful elaboration of a plant and process for the complete purification of flue gases was one of the outstanding achievements in chemical engineering during the last few years. The work leading up to the design of plant and devising the process presented many problems in physical chemistry. Not the least was the prevention of incrustation from supersaturated solutions. He had pointed out six years ago the inexpediency of discharging the spent liquors into water courses and strongly advocated a cyclic, non-effluent system. He was also of opinion that the CaSO_3 primarily formed should be completely oxidised to CaSO_4 . This could be done without difficulty and would eventually lead to the commercial utilisation of the product of reaction in form of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

Mr. G. Nonhebel (*Billingham*), in reply, said : It would be perfectly possible to use a straight through water system with the process provided sufficient water was available to irrigate the packing, and that water contained sufficient bicarbonate to neutralise the absorbed SO_2 . Addition of lime to the inlet water in absence of the dissolved CO_2 present in the recirculating system gives a scale of CaCO_3 on the pipes and packing. Finely ground chalk is probably not sufficiently reactive. The separation of the dust from the used water of such a straight through system would undoubtedly cause difficulties, owing to the large volume of water involved.

One use to which the solids collected by the system could be put would be the manufacture of plaster. It would be necessary to incorporate in the liquor recirculating system an oxidiser of the type mentioned by Dr. Lessing in order to convert all the calcium sulphite to sulphate. With stoker firing the product would then contain 85-90 per cent. $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Until large-scale plants are running, however, it is not possible to predict how the particle size will vary with the inevitable and frequent variations in load experienced in power stations, and reasonable uniformity is essential for such a product.

With very large plants there might be an economic case for utilisation of the mixture of ash and CaSO_3 , etc., for the production of cement and sulphuric acid.

¹ *J. Inst. Fuel*, 1935, 119.

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IONIC RADII AND HEAT OF HYDRATION.

BY ANDR. VOET.

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1. If the reciprocal values of the heats of hydration of the ions of the alkaline metals¹ are plotted against the radii, as given by Pauling,²

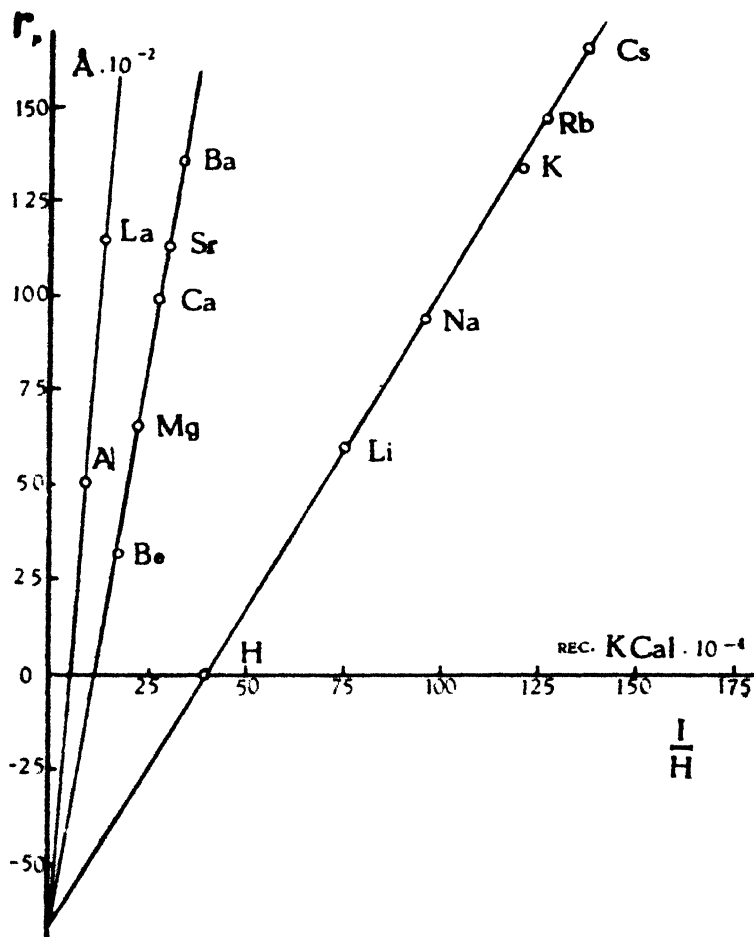


FIG. 1.

a straight line is obtained. An analogous relation occurs for the ions of the alkaline earth metals³ as well as for trivalent ions (Fig. 1).

¹ Van Arkel and de Boer, *Chemische Binding*, Amsterdam, 1930.

² L. Pauling, *J. Am. Chem. Soc.*, 1926, 49, 765.

³ Data from *Handbuch der Physik*, 1934, 24^{II}—

A similar result was obtained by Webb,⁵ who calculated a difference of about 0.53 Å. by the use of electrostriction data.

Since the ion in solution may be defined as a cavity into which the medium cannot penetrate, whilst in crystals the radii are calculated from the distances of the ions, a difference between the two values does not seem unnatural. In the case of an ion in water, the electric dipole, situated in the water molecule, will never approach closer than a fixed distance to the ion, defined as above. Therefore it does not seem improbable that the length of 0.65 Å., which is independent of the nature of the ion, is closely related to the shortest distance between the ion and one of the poles (in this case evidently the negative one) of the water dipole. In this trend of thought a general extension of the Born-Bjerrum equation (2) of the following form may be introduced :

$$H = \frac{Ne^2z^2}{2(r+b)} \left[1 - \frac{1}{D} + T \frac{\partial}{\partial T} \left(\frac{1}{D} \right)_P \right], \quad (3)$$

where b is a constant for each medium, dependent on its molecular structure.

4. Many objections have been brought against the validity of the Born-Bjerrum equation. Calculations carried out on the basis of Debye's theory of dielectrics⁶ showed that the dielectric constant of the medium decreases in the vicinity of an ion by electrical saturating effects.^{6,7} Recent publications,⁸ however, prove that this theory in its original form is inadequate in the case of liquid water where, for instance, the theoretical saturating effect is 3500 times the observed at a field strength of 100,000 volts/cm. It is possible, therefore, that in the Born-Bjerrum equation no electrical saturating effect has to be taken into account.

The energy of electrostriction, which has been calculated by Webb,⁵ may be neglected.

One effect which has to be taken into account is the influence on the ion of the electric field of the molecules of the medium. As the negative ions have a high polarisability, the hitherto unknown energy of interaction between anions and water dipoles should be added to the energy calculated from the Born-Bjerrum equation. This interaction might also have an effect on the radius of the anions.

This explains why the empirical relationship between the ionic radii and the heats of hydration of anions does not accord with the modified Born-Bjerrum equation (3). The energy of interaction of cations and water molecules may be neglected, owing to the small polarisability of the positive ions. This difference is emphasized by the eccentric position of the dipole in the water molecule.

Recent publications⁹ indicate that the Born-Bjerrum equation is totally inadequate in the case of non-aqueous solutions. Since a proper separation of the hydration energy data of salts into ionic data is impracticable, a direct test of equation (3) seems impossible; as however, it contains a molecular constant, which is different for each medium; it does not seem incompatible with the experiments.

⁵ J. Webb, *J. Am. Chem. Soc.*, 1926, 48^{II}, 2589.

⁶ P. Debye, *Polar Molecules*.

⁷ A. Gyemant, *Z. Physik*, 1924, 30, 240.

⁸ J. Malsch, *Physik. Z.*, 1929, 30, 837; J. D. Bernal and R. H. Fowler, *J. Chem. Physics*, 1933, 1, 515; P. Debye, *Physik. Z.*, 1935, 36, 100, 193.

⁹ F. A. Askew et al., *J. Chem. Soc.*, 1934, 1368; K. Miščenko, *Acta Physico-chimica U.R.S.S.*, 1935, 3, 693.

Summary.

1. A linear relationship has been established between ionic radii and reciprocal heats of hydration of positive ions.
2. An explanation has been proposed on the basis of the electrostatic theory.
3. A modification of the Born-Bjerrum equation is introduced and its validity discussed.

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X-RAY STUDIES OF THE COAGULATION PROCESS OF COLLOIDAL GOLD.—PART I.

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Received 6th April, 1936.

Introduction.

The process of coagulation in lyophobic sols has often been investigated with regard to the relation between the rate of coagulation, "zeta" potential and the electrolyte concentration respectively. The experiments have shown that there exists a range of charges where each collision between two particles in solution is unelastic, *i.e.*, if these particles touch they adhere to one another permanently.¹ This range is the so-called region of rapid coagulation.² With less discharged particles not every collision is unelastic and only a fraction cause a permanent adhesion; this is the region of slow coagulation.³ According to von Smoluchowski,² in the rapid region, the rate of coagulation is independent of the concentration of the coagulating electrolyte; this has also been proved by experiment.¹ In the slow region, the rate of coagulation is mainly dependent on the "zeta" potential of the particles.

The primary particles in a gold sol are themselves single crystals,⁴ while the secondary particles are assumed to be an irregular agglomerate of unchanged primary particles.

The above-mentioned kinetic investigations did not furnish information as to the nature of the secondary particles, which were generally assumed to adhere irregularly and to be unchanged in size or shape.⁶ This question was not investigated until recent years owing to the lack of available optical and X-ray experimental methods, the only means by which information can be obtained. With optical methods it has been shown that, during the course of a very slow coagulation, the primary particles may adhere somewhat regularly.⁶ Similarly, in some instances where coagulation occurs at the air-liquid interface, such a regular coagulation may become very pronounced with high-speed stirring.

¹ Freundlich, *Kapillarchemie*, 1932, 2, 140 *et seq.*

² von Smoluchowski, *Physik. Z.*, 1916, 17, 557; *Z. physik. Chem.*, 1918, 92, 129.

³ Freundlich, *Kapillarchemie*, 1932, 2, 147 *et seq.*

⁴ P. Scherrer, Zsigmondy, *Kolloidchemie*, 3rd edn., 1920, p. 387.

⁵ Zsigmondy, *ibid.*, p. 119, *cf.* p. 409.

⁶ H. Kautsky in a paper by Zocher, *Z. physik. Chem.*, 1921, 98, 319.

For example, the sols of copper oxide and Goethite do not initially show stream double refraction; this, however, appears after coagulation by stirring, but never after rapid coagulation by electrolytes.⁷ Thus, one must assume that the primary particles adhere more regularly during the very slow coagulation brought about by stirring, forming larger, non-spherical aggregates. With optical means it cannot be established, whether this particle growth is due to crystallisation or only to a stable oriented arrangement of unchanged primary particles.*

In 1921, Scherrer,⁴ using the Powder method of X-ray analysis showed that colloidal gold and silver possess the same structure as the macroscopic crystals. This was confirmed by Björnstaahl.¹⁰ Scherrer also showed that it is possible to determine the size of small particles from measurement of the breadths of the diffraction lines. The principle of this method was used by Stoll¹¹ who concluded, without giving any experimental details, that the particle size of colloidal gold increased upon coagulation. In 1931, Scherrer and Staub¹² showed that the coagulation of highly-dispersed gold sols carried out in the rapid region, produces first an irregular agglomeration of the primary particles, the individual crystals forming these particles having the same size as those of the original sol. Crystallisation of the primary particles could be brought about either by extensive drying of the coagulate or by allowing it to stand in the electrolyte solution. This process proceeded more rapidly at higher temperatures, was greatly hindered by the addition of a protecting agent and did not take place to the same extent with dialysed sols (probably due to some protective action on the particles).

The size of the ultimate crystallite can only be obtained by an X-ray method; other methods give only the magnitude of the secondary particle aggregate and do not permit conclusions to be drawn regarding its intimate structure.

Since Professor Scherrer† does not propose to extend the work reported by Scherrer and Staub,¹² it was decided to carry out a more systematic X-ray study of the coagulation process. One of the main questions to investigate was how far the crystallisation is connected with those functions which are usually linked up with coagulation, namely the

* The latter possibility must be considered, since many crystalline colloidal particles show a tendency to orient regularly and to form approximately regular aggregates; e.g., in concentrated colloidal solutions of many oxides and dyestuffs containing non-spherical (rod or plate-shaped) particles, the formation of regular aggregates of "tactoids" may easily be seen. If, for example, a drop of an old, concentrated V_2O_5 sol is observed microscopically between crossed Nicols and evaporation is avoided, the "tactoids" appear as bright double-reflecting spots in the course of time. These tactoids are not considered to be crystals since they may be readily dispersed by moving the cover glass on the microscope slide, but form again after a short interval. The ultramicroscope shows that the individual particles forming the "tactoids" have a slow rotary Brownian movement.⁸ The directing forces responsible for the formation of the "tactoids" seem to be specific, since in a sol containing particles of two widely different substances (e.g., V_2O_5 and benzopurpurin) "tactoids" of both substances are formed side by side.⁹

⁷ Freundlich and co-workers, *Z. physik. Chem.*, 1925, 115, 203; 1926, 124, 155; 1928, 139, 368; 1931, 157, 325.

⁸ H. Freundlich, *Kapillarchemie*, 1932, 2, 55 et seq.

⁹ H. Freundlich, O. Enslin and K. Söllner, *Protoplasma*, 1933, 17, 489.

¹⁰ Y. Björnstaahl, *Inaug. Diss., Uppsala*, 1924, p. 158.

¹¹ Stoll, *Arch. Sci. Physiques (Genève)*, 1921, 3, 347.

¹² P. Scherrer and H. Staub, *Helv. Physic. Acta*, 1930, 3, 457; *Z. physik. Chem. A*, 1931, 154, 309.

† Private communication to Professor Freundlich.

charge of the particles and the rate of coagulation. In addition, it was decided to investigate the effect, on the rate of crystallisation, of the concentration of the coagulating electrolyte and the period the coagulate was allowed to remain in the electrolyte solution.

The mechanism of this particle growth, as determined by X-ray methods, is not yet definitely established, but many arguments may be advanced for the view that it differs from that usually assumed for relatively insoluble substances such as barium sulphate and calcium carbonate. Here, owing to their higher solubility, the smaller crystals are dissolved and the so-formed ions or molecules separate out of solution on the larger crystals already present. For this reason stable hydrosols of these substances cannot be obtained.

Since gold hydrosols are stable without increase in particle size for practically unlimited periods, but grow rapidly upon coagulation, a similar mechanism of the particle growth seems improbable. It appears more likely that in this and similar cases of substances with an extremely low solubility, the primary particles grow together (i.e., show mass crystallisation) without undergoing intermediate solution, when brought close enough to each other.*

There has never been any doubt that coagulated particles are close to each other. It is a well-known fact that the dull powders of precipitated gold and silver readily turn macrocrystalline and metallic-looking when gently touched; with higher pressures they form solid metallic masses. These processes are much more rapid at higher temperatures; e.g., Scherrer and Staub¹² found an increase from 69 Å. to 390 Å. on heating a dried gold coagulate for a short time at 300° C.; here the interaction of traces of a liquid solvent seems improbable. Further arguments may be advanced in favour of this view, e.g., the extremely high diffusion coefficient of metallic atoms within metals^{15 16} and the rapidity of the particle size increase after coagulation and its hindrance by protecting agents such as gelatin.

For the above reasons it seems probable that the coagulated gold particles unite as such, as soon as they touch each other bodily.† It is then possible for the high atomic mobility within the crystal lattices (which may reasonably be assumed to be much higher at the surfaces ‡) to come into action. Considerations of the structure of "tactoids" seem to establish that the crystals can be brought into suitable positions by the Brownian movement and by molecular forces. The action of such directing forces was realised by Lehmann¹⁷ when investigating, microscopically, the coalescence of crystals of *p*-azoxy ethylbenzoate;

* Obviously this view was not unfamiliar to Zsigmondy¹³ and was the basis of the investigations of Scherrer^{4 12} on the crystallisation of colloidal gold. Moreover, it seems reasonable to assume that the different tendency of different substances to show (mass) crystallisation is related to the ultimate difference between reversible and irreversible colloids—a difference which was greatly emphasised by Zsigmondy.¹⁴

¹² Zsigmondy, *Kolloidchemie*, 4th edn., 1920, p. 19.

¹⁴ *Ibid.*, p. 29.

† This is also necessary for the assumption that the particle growth is due to some localised electrolytic action. (In our opinion, very unlikely.)

‡ This phenomenon, afterwards found to be very common, was first investigated carefully by Volmer and Estermann.¹⁸

¹⁵ W. Jost, *Z. physik. Chem. B*, 1932, 16, 123.

¹⁶ W. Seith and A. Kiel, *ibid.*, 1933, 22, 350.

¹⁷ O. Lehmann, *Flüssige Kristalle*, Leipzig, 1904, p. 37.

¹⁸ M. Volmer and J. Estermann, *Z. Physik*, 1921, 7, 13.



FIG. 1. Original sol. Protected, dialysed and evaporated. 35 Å.



FIG. 2. Rapid coagulation. Protected immediately after coagulation. 43 Å.



FIG. 3. 0.04 millimols per litre. Protected immediately after addition of electrolyte, dialysed and evaporated. 50 Å.



FIG. 4. As Fig. 3, but protected after 6 hours. 65 Å.



FIG. 5. As Figs. 3 and 4, but protected after 48 hours. 100 Å.

[See page 1307.



FIG. 6. - Rapid coagulation in negative region. 0.19 millimols per litre. Coagulate stood 24 hours in electrolyte solution. 120 A.



FIG. 7. - Rapid coagulation in positive region. 240 millimols per litre. Coagulate stood 24 hours in electrolyte solution. 130 A.



FIG. 8. - Rapid coagulation in negative region. 0.14 millimols per litre. Protected 1 minute after the addition of electrolyte. 98 A.



FIG. 9. - As Fig. 8, but protected after 20 minutes. 112 A.

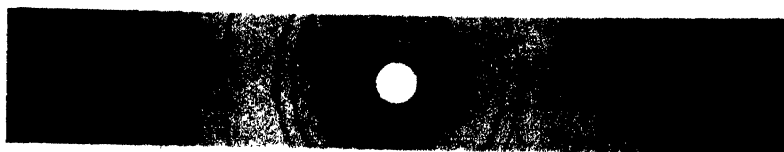


FIG. 10. - As Fig. 7, but coagulate allowed to remain 216 hours in the electrolyte solution. 135 A.

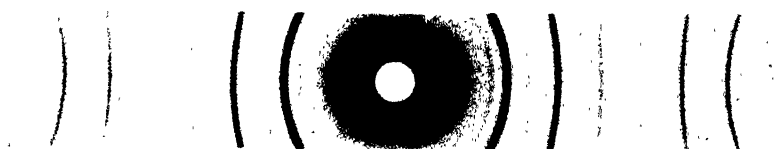


FIG. 1. Magnesium Oxide.

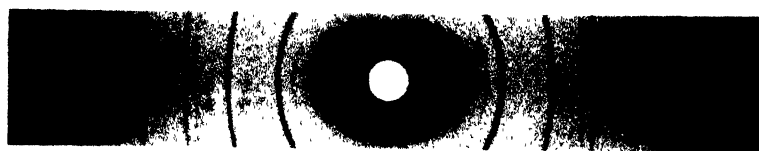


FIG. 2. Magnesium Oxide on lead glass

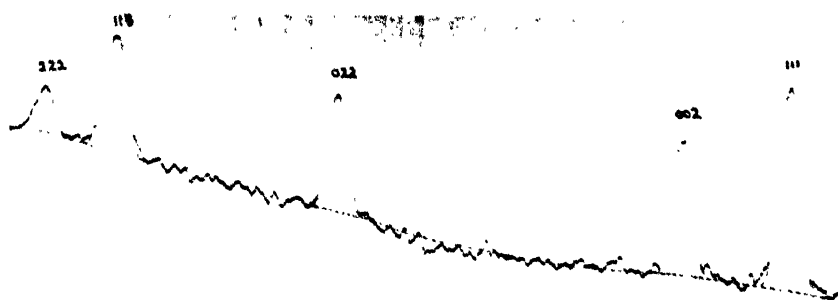


FIG. 4. Photometer record of particles 130 Å. Planes 111 to 222 inclusive.

See page 1313.

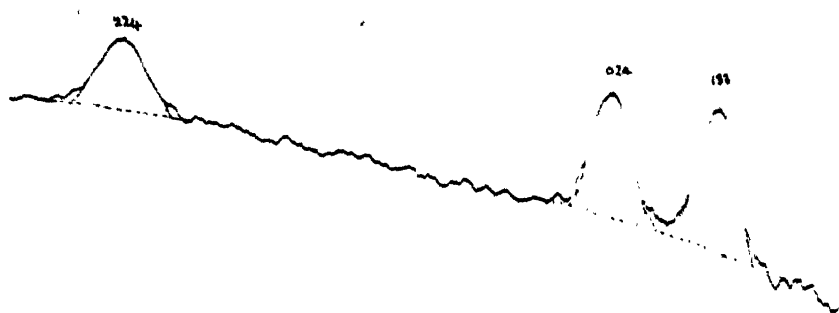


FIG. 5 As Fig. 4 but planes 111, 024 and 224



FIG. 6 Colloidal gold; protected and evaporated 35 Å



FIG. 7 As Fig. 6 but on lead glass

he observed that as two crystals touched one another they were oriented parallel and finally coalesced to form a single crystal.*

A gold sol was chosen for the following investigations because, in addition to the X-ray and colloidal points of view previously mentioned, effects due to solubility can hardly be considered, so that one may hope to get some insight into the processes which occur during and after the aggregation of the primary particles in the process of coagulation.

The particle size values reported in this paper are only intended to be relative, since it is pointed out in Part 2, which deals with the X-ray technique, that the absolute values may be in error by a factor of 2.

Experimental.

Preparation of the Gold Sol.

16 litres of the sol were prepared by the phosphor-gold method as modified by Scherrer and Staub.¹² Conductivity water, obtained from a CO₂-free Pyrex still was used for the preparation of all the solutions. All vessels were made of Jena glass and were thoroughly cleaned by steaming out for several days. The sol container was of 20 litres capacity. The prepared sol, which is about four times more concentrated than the usual phosphor-gold sol, was slightly acid showing a $p_H = 6.3$.

Prior to any experiments, the sol was allowed to stand for 12 weeks. Its particle size was found to be constant throughout the work within the experimental error of the determinations (about 10 per cent.).

The undialysed sol was used for the coagulation experiments in order to obviate any possibility of protection of the particles occurring by the passage of protecting substances out of the dialysing membrane. Such an effect was observed by Zsigmondy¹³ and has been discussed by Scherrer and Staub.¹²

Particle Size of the Original Sol.

A portion of the sol was protected with pure bacteriological gelatin, dialysed in a cellophane sac against frequent changes of conductivity water for 48 hours and finally evaporated down *in vacuo* at 25° C. There was then no trace of potassium, chloride or phosphate ions. The evaporated sample was readily soluble in water, giving the original deep-red colour of the sol. Preliminary experiments on the undialysed sol gave extraneous diffraction lines due to the above-mentioned impurities formed during the preparation of the sol. The diffraction diagram of the original sol is shown in Fig. 1. The particle size being 35 Å.

Coagulation Experiments.

All coagulations were carried out by the addition, from a microburette, of varying volumes of solutions of aluminium chloride. This electrolyte was chosen because small concentrations readily reverse the charge on the particles and thus the whole region of coagulation can be investigated with one electrolyte. All the reported values of electrolyte concentrations refer to the total volume of the solution after the addition of the electrolyte and are expressed in millimols of aluminium chloride per litre.

The rate of coagulation was judged from the time of the colour change from red to blue after the addition of electrolyte. No exact measurements

* Here, the cementation of the two crystals may be partially brought about by the dissolved substance present.¹⁷

¹² Zsigmondy-Thiessen, *Das Kolloides Gold*, p. 48.

Experimental Results.

Region of Slow Coagulation.

At an aluminium chloride concentration of 0.04 millimols/litre no visible colour change appeared even after 48 hours. The lowest concen-

TABLE I.

Electrolyte Conc. Millimols/Litre.	Charge.	Rate of Colour Change.	Particle Size in Å after :		
			Immediately.	6 hrs.	48 hrs.
0.04	(---)	nil	50	65	100
0.06	(---)	v. slow	70	97	112

tration where a colour change appeared after several hours was 0.06 millimols/litre. In both cases, three samples were protected (1) immediately after the addition of the electrolyte, (2) after 6 hours, and (3) after 48 hours. The results are shown in Table I.

Figs. 3, 4, and 5 respectively show the X-ray diagrams corresponding to a concentration of 0.04 millimols/litre. The sharpening of the diffraction lines, on allowing the solution to stand, is readily observed.

The dependence of the rate of crystallisation on the electrolyte concentration, for a constant time of standing (24 hours) is apparent from Table II(a).

TABLE II.

Electrolyte Conc. Millimols/Litre.	Charge.	Particle Size in Å.
(a) Slow Coagulation.		
0.09	(---)	77
0.10	(---)	98
0.11	(---)	98
0.11 ₆	(---)	83
0.12 ₄	(---)	96
0.13	(---)	90
0.13 ₆	(-)	109
(b) Rapid Coagulation.		
0.14	(-)	121
0.15	(-)	127
0.16 ₆	(-)	129
0.16 ₆	(-)	124
0.17	(-)	130
0.18	(-)	123
* 0.19	(-)	120
0.25	(+)	116
0.38	(++)	122
0.50	(++)	121
0.75	(++)	129
1.0	(+++)	120
5.0	(++++)	126
15.0	(++++)	131
† 24.0	(++++)	130
40.0	(++++)	132
83.0	(++++)	129
143.0	(++++)	128
222.0	(++++)	130

Region of Rapid Coagulation.

As above, the coagulates were allowed to remain in the electrolyte solution for a period of 24 hours; coagulates above a concentration of 0.17 millimols/litre settled out rapidly but below this concentration they were centrifuged out with difficulty and contained relatively large amounts of gelatin. These results also appear in Table II(b).

The Dependence of the Rate of Crystallisation on the Time the Coagulate is allowed to remain in the Electrolyte Solution.

The results in the region of slow coagulation have already been given in Table I.; those in the region of rapid coagulation are given in Table III.

* Fig. 6.

† Fig. 7.

TABLE III.

Conc. m-mols/ litre.	Charge.	Rate of Settling.	Particle Size in Å after :							
			Immedy.	1 min.	20 mins.	4 hrs.	24 hrs.	48 hrs.	96 hrs.	216 hrs.
0.14	(-)	nil	—	98 *	112 †	116	121	—	—	125
0.25	(+)	rapid	—	—	—	—	116	122	130	129
5.0	(+++)	rapid	—	100	—	—	126	131	131	132
24.0	(+++)	rapid	—	—	—	—	130	—	—	135‡
143.0	(+++)	rapid	43	—	—	—	128	127	126	128

* Fig. 8.

† Fig. 9.

‡ Fig. 10.

The Effect of Drying the Coagulate.

Two unprotected coagulates of sizes 120 Å. and 130 Å. respectively were dried for 12 hours of P_2O_5 at a pressure of approximately 1 mm. Hg. The final particle size values of both coagulates were indistinguishable from the original values. Similar results were observed by Scherrer and Staub¹² who found that two samples of 69 Å. and 138 Å. respectively also gave, within experimental error, the same values, after drying, as those of the original particles. They explained the failure of these large particles to show any further crystallisation by assuming that some protective action had taken place; this may, however, be explained in a different way (see below).

Discussion.

Crystallisation of the primary particles occurs even though there has been no visible colour change (Table I.),* but when a colour change takes place the crystallisation proceeds more rapidly. As previously mentioned, these values are higher than the actual values at the time of addition of gelatin to the solution, since crystallisation proceeds during dialysis, even after the particles are protected. The values of 50 Å. and 70 Å. respectively in Table I. are not in agreement with the value of 43 Å. obtained in the rapid region of coagulation (Table III.), where the particles are quickly separated from the electrolyte solution by centrifuging.

From Table II(a.), it is evident that, in the region of slow coagulation, for a constant period of standing in the electrolyte solution, the rate of

* Bearing in mind that this visible method is very rough, this increase may readily be explained by the fact that low electrolyte concentrations favour the formation of small aggregates, probably with many of the primary particles remaining unchanged. In the normal course of events (*i.e.*, when the rate of coagulation is greater than the rate of crystallisation of the primary particles) the appearance of a blue colour indicates the formation of irregular, loose-packed aggregates. Owing to the size of these aggregates, both the state of loose-packing and the blue colour may still remain even after considerable internal crystallisation has taken place. However, crystallisation of the very small aggregates formed at very low electrolyte concentrations, may cause both the state of loose-packing and the blue colour to disappear. Such a sol, although possessing greatly increased particle size, may still be red, since gold sols with primary particles up to 1200 Å. are often this colour.¹⁰ ²¹ Since, in the experiments recorded in Table II(a.), the blue colour never appeared, the results seem to indicate that the rate of crystallisation is greater than the rate of coagulation.

²⁰ Zsigmondy-Thiessen, *Das Kolloide Gold*, p. 120 *et seq.*

²¹ Zsigmondy, *Kolloidchemie*, 3rd edn., 1920, p. 160 *et seq.*

crystallisation depends directly upon the electrolyte concentration and thus on the rate of coagulation.

Table II(b). shows that under the same conditions in the region of rapid coagulation, the extent of the crystallisation is equal and independent of the concentration of the coagulating electrolyte—both with negative and positive coagulants.

The combined results indicate that the crystallisation is directly dependent on the rate of coagulation; no abnormal effect was observed near the iso-electric point, such as might be expected where the electrokinetic charge of the particles is zero.

The results of Table III. and to some extent those of Table I. show that the maximum crystallisation takes place within a very short time after the addition of the electrolyte, in the rapid region of coagulation. Although this process continues with increasing time of standing in the electrolyte solution, the relative speed rapidly diminishes. The results also confirm those of Scherrer and Staub,¹² namely rapid coagulation causes at first an irregular agglomeration of the primary colloidal particles (Fig. 2) and, thus, also the basic ideas of the von Smoluchowski theory of rapid coagulation.² These irregularly aggregated (or at least incompletely oriented) particles are afterwards oriented (mainly rapidly), forming bigger crystalline units.

These results seem to favour the assumption of a mass crystallisation phenomenon, as set out in the introduction. Thus the close parallelism between rate of coagulation and particle growth can be understood on the same basis, namely the interaction of the attracting (and directing) and repelling forces between the particles.

It may be said, especially against the results in the rapid region, that the size of the crystals, as found by the X-ray method, may be quite different from the actual size of the masses of material bound together by primary linkages. The formation of an extended skeleton could not be detected by X-ray methods. Since the particles are not of uniform size and are not necessarily regular in shape, only a limited number of particles would be able to adhere regularly and without any skeleton formation.* Furthermore, a defective arrangement or incomplete orientation of the crystals would affect the diffraction line breadths and lead to illusory values for the size of the crystals formed by aggregation. In this way the limiting value of 120 Å.-130 Å. (Table II(b).) and the failure of the particles to show any further crystallisation when dried, could be easily understood. Further investigations, both by X-ray and ultra-microscopic methods, with sols of different primary particle size, prepared either by different methods or with a different substance (*e.g.*, silver) may overcome these difficulties.

The authors wish to express their thanks to Professor F. G. Donnan, C.B.E., F.R.S., for his interest in the work; to Professor H. Freundlich for his valuable advice; and to Mr. G. S. Hartley for the supply of conductivity water.

Summary.

Coagulation of a highly-dispersed gold sol causes the primary particles to form, at first, an irregular agglomerate, the individual crystal size of which is the same as that of the original sol.

* Cubes of different sizes or octahedra (the generally assumed shape of colloidal gold particles) of equal sizes cannot be packed together in space without interstices.

Crystallisation of the primary particles may be brought about by allowing the coagulate to remain in the electrolyte solution.

The crystallisation is dependent on the rate of coagulation and is constant over the whole region of rapid coagulation. In this latter region the maximum growth takes place very rapidly.

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X-RAY STUDIES OF THE COAGULATION PROCESS OF COLLOIDAL GOLD. PART II. X-RAY EXPERIMENTAL TECHNIQUE.

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The X-ray method of particle size determination depends on the line broadening observed in the Powder diffraction diagram when the individual crystal size falls below approximately 10^{-8} cm.

A connection between the breadths of the diffraction lines and the size of the particles under investigation was first pointed out by Scherrer¹ who derived the following equation for cubic crystals:—

$$B = 2\sqrt{\frac{\log_e 2}{\pi}} \cdot \frac{\lambda}{A} \cdot \sec \theta + b, \quad (1)$$

where: B is the line breadth in angular measure; A the particle size (cube edge); θ the glancing angle of X-ray reflection; λ the wavelength of the incident radiation; b a constant depending on the specimen diameter; and the definition of the incident radiation.

The line breadth is generally defined as the ratio of the integrated X-ray intensity across the diffraction line, to the maximum intensity, i.e., $B = 1/I_{\max} \int I \cdot dx$, where I is the intensity and x the lateral distance in the scale of the diagram. This measurement is somewhat difficult to make in practice and it is more usual to measure the line breadth at half the maximum intensity. The former method, however, tends to give values which are more independent of the shape of the intensity curve of the diffraction line than the latter.

From equation (1), it is apparent that the relation between B and $\sec \theta$ should be linear and the slope of this graph is equal to $2\sqrt{\frac{\log_e 2}{\pi}} \cdot \frac{\lambda}{A}$; from which the particle size A can be calculated. The intercept on the B axis gives the value of b .

Two of Scherrer's assumptions (namely parallel incident radiation and transparent sample) are difficult to realise in practice. Brill² and Cameron³ have pointed out that with *divergent* radiation and transparent samples, the line breadths at small angles become very large

¹ P. Scherrer, Zsigmondy, *Kolloidchemie*, 3rd edn., 1920, p. 394.

² R. Brill, *Z. Krist.*, 1928, **68**, 387.

³ G. H. Cameron, *Physics*, 1932, **3**, 57.

Fig. 1, *i.e.*, the slope of the $B/\sec \theta$ graph is very small or even negative. If, however, the sample is strongly absorbing, either in itself or is made so by coating it on a lead glass rod, the two defects oppose one another with a marked reduction in the central line breadths (Fig. 2). Thus, in favourable circumstances, the Scherrer condition (that B is a linear function of $\sec \theta$) may accidentally be realised.

Equations, similar to that of Scherrer, have been proposed by Seljakow⁴ and Randall, Rooksby and Cooper;⁵ these, which are based on assumptions similar to those outlined above, differ only in the value of the numerical constant.

Von Laue⁶ has given a more general theoretical analysis where the crystals are not confined to those of the cubic system. The radiation was assumed to be purely divergent:

$$B = \frac{\pi \cdot \frac{\omega}{\eta} \cdot \left(\frac{r}{R}\right)^2 \cos^3 \theta}{\sqrt{1 + \left(\frac{\omega r}{\eta R} \cdot \cos^2 \theta\right)^2} - 1}, \quad (2)$$

where: B is the absolute corrected value of the line breadth in angular measure; θ the angle of reflection; ω a constant (0.55); R the camera radius and r the specimen radius.

η is a quantity related to the particle size by a complex expression which, for cubic crystals, reduces to:—

$$\eta = \frac{\lambda}{4\pi A}, \quad (3)$$

where λ and A have the same significance as before.

Brill's Modification of von Laue's Theory.

Brill² has shown that, for a completely absorbing solid cylindrical sample and for infinitely large particles, the experimental line breadths B' will be connected with the B used by von Laue by the following expression:—

$$B = \frac{B'}{\sin^2 \theta}. \quad (4)$$

Brill's procedure was to correct the measured line breadths by equation (4); reduce to absolute values in angular measure and, for cubic crystals, to calculate the particle size by equations (2) and (3). Finally, since complete absorption may not be obtained in a thin layer at the surface, the calculated particle sizes from each diffraction line were plotted against $\sin^2 \theta$ and extrapolated to find the size at $\sin^2 \theta = 1$, since at $2\theta = 180^\circ$ absorption is assumed to have no effect.

This procedure has been criticised by Cameron;³ *e.g.*, the accuracy of the final result depends on the presence of one or more diffraction lines at large angles of reflection, which is often difficult to achieve; in addition, the correction for absorption (equation 4) was developed for parallel radiation, while von Laue's theory was developed for purely divergent radiation; moreover, the correction was developed for sharp lines, *i.e.*, the effect of absorption on the line broadening due to small particles was

⁴ Seljakow, *Z. physik. Chem.*, 1925, 31, 439.

⁵ Randall, Rooksby and Cooper, *Z. Krist.*, 1930, 79, 196.

⁶ M. von Laue, *ibid.*, 1926, 64, 115.

neglected. However, he concluded that, while in many cases, the final results may err by a factor of 2 in absolute value, the methods of Scherrer, von Laue and Brill were capable of arranging a series in the correct order of size with considerable precision.

The Brill and Pelzer Total Absorption method ⁷ was not used in the experimental work reported below owing to the difficulty of coating thin, even layers of gelatinous samples on the lead glass rod. It is essential that this layer is thin otherwise the line breadths at low angles tend to be excessively large, while an uneven layer produces lines whose intensity, on either side of the centre, is unequal (*cf.* Fig. 7).

Experimental.

The X-ray diffraction diagrams were obtained in a Powder camera of 28.29 mm. radius, with a pinhole 1 mm. diameter. Cu K α radiation was

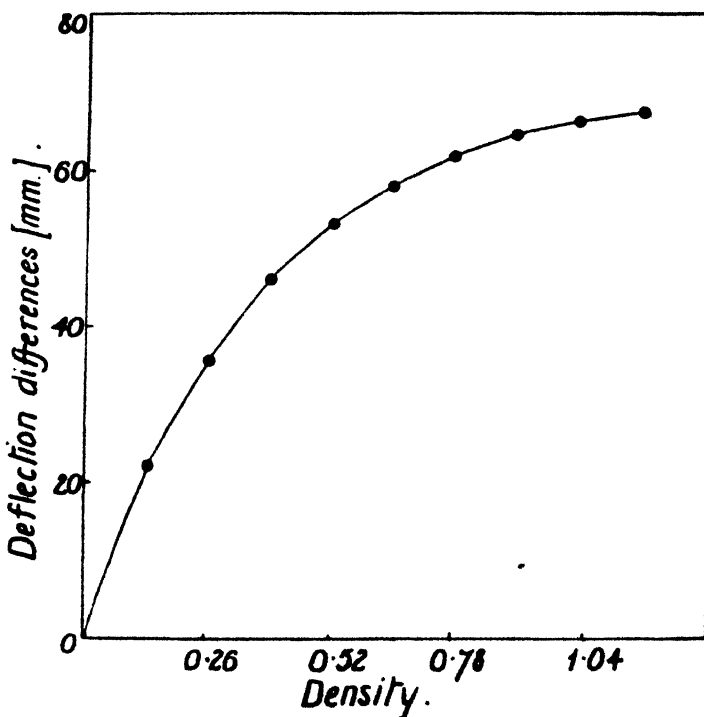


FIG. 3.

used throughout; the β component being eliminated by means of a Ni filter. The average exposure time (at 40 Kv and 20 Ma) was 15 minutes, which was found to produce line densities falling within the limits (0.2 and 0.65) required for the correct intensity interpretation of the films. All the specimens were supported in thin collodion tubes ranging in diameter between 0.4 and 0.8 mm.

The difference in photographic contrast between various films was minimised by utilising a standard time of development (4 minutes at 17° C.) with a metol-hydroquinone developer; the film container was rocked to ensure uniform development.

All films were photometered on a Zeiss self-registering microphotometer.

⁷ Brill and Pelzer, *Z. Krist.*, 1930, **74**, 147.

Determination of the Intensity-Deflection Relation.

For the correct intensity interpretation of the diffraction lines it is essential to know the relation between the intensity of the X-ray beam producing a given deposit on the film and the deflection of the photometer fibre when this spot is photometered. The density D of a given deposit on the film may be defined by the relation $D = \log_{10} \frac{I_0}{I}$; where I_0 is the intensity of a beam of light from a constant source after it has passed through the film exposed to the general radiation on either side of the deposit and I is the intensity after passing through the deposit itself.

A great deal of work has shown that, for densities up to about 0.8, there is a linear relation between the X-ray intensity producing a given deposit on the film and the density of that deposit.^{9, 9, 10, 11, 12, 13}

The relation between the microphotometer deflection and density was determined by placing 1, 2, 3 . . . strips of equally exposed and developed film in the path of the light falling on the photocell and measuring the corresponding deflection. The density of each strip, from an independent calibration, was 0.132 ± 0.007 . The ordinates of the experimental graph (Fig. 3) represent the differences in deflection $(y_0 - y_1)$; $(y_0 - y_2)$. . . where y_0, y_1, y_2 are the deflections corresponding to 0, 1, 2 . . . strips of film. In reality this curve is exponential, however, between densities of approximately 0.2 and 0.65 (deflections between 20 and 60 mm. or differences of 40 mm.) it is nearly linear; this assumption, though not strictly accurate, greatly simplifies the line breadth determinations, the error involved being only a few per cent. as is seen from Table I. of three typical uncorrected line breadths (in linear measure) determined by various methods:

I. By measurement of the "half intensity width" assuming the above linearity (for further details see below).

II. As I., but measuring on the more correct log (deflection) curve.

III. As I., but measuring on the photometer curve replotted in terms of density by interpolation from the density-deflection curve.

IV. By measurement of the line breadth from the definition

TABLE I.

Planes	I	II	III	IV
133	1.20	1.17	1.18	1.23
024	1.11	1.13	1.14	1.24
224	1.53	1.54	1.51	1.55

The values are expressed in millimetres.

$$B = \frac{1}{I_{\max.}} \int I \cdot dx$$

using Miles's method.¹⁴

Relative variations do not affect the results of Part I., which are only intended to convey relative orders of magnitude.

Measurement of the "Half-Intensity Width."

In order to obtain a reasonably high linear magnification of the curves, the diffraction diagrams were photometered in two separate parts; namely the planes 111 to 222 inclusive and 133, 024 and 224 with magnifications of 6.55 and 9.46 respectively. The omission of the 004 plane is of no

⁹ Friedrich and Koch, *Ann. Physik.* 1914, **45**, 399.

⁹ Glocker and Traube, *Physik. Z.*, 1921, **22**, 345.

¹⁰ Bouwers, *Z. Physik.* 1923, **14**, 374.

¹¹ Busse, *Physik. Z.*, 1925, **34**, 11.

¹² Martin and Lang, *Pro. Roy. Soc. A*, 1932, **137**, 199.

¹³ F. D. Miles, *Trans. Faraday Soc.*, 1935, **31**, 1452.

¹⁴ F. D. Miles, *Phil. Trans. A*, 1935, **235**, 124.

consequence as it was, in almost every case, too weak for any accurately measurable deflection to be obtained from it. Two typical photometer records from a diffraction diagram corresponding to a particle size of 130 Å. (Fig. 7 in Part I) are shown in Figs. 5 and 6.

The "Half-Intensity Width" of the diffraction lines is represented by the line breadth at half the difference between the background and peak deflections; both the latter being measured from zero deflection (*i.e.*, with no light falling on the photocell). Where necessary, these values were corrected for slope of the background by Brill's formula,³ yielding final values of b . The actual line breadth (b') in linear measure is then b/M , where M is the photometer magnification.

For the experimental use of the Scherrer equation the values of b were converted into absolute angular measure B'_{abs} , by division by the camera radius. For the Brill method the values of b' were corrected:

(a) where necessary, for asymmetry of the photometer curves, by Brill's formula.³

(b) For absorption by equation 4. These values were finally converted into angular measure B_{abs} , as above.

Application of the Scherrer Equation.

The particle size A was calculated, using the method of least squares, from the following equation:—

$$A = \frac{2\lambda \sqrt{\frac{\log_e 2}{\pi}} \left[n \sum \sec^2 \theta_n - \sum \sec \theta_n \right]}{n \sum B'_{n(\text{abs})} \sec \theta_n - \sum B'_{n(\text{abs})} \sum \sec \theta_n}$$

In view of the strongly absorbing properties of gold and of the divergent X-ray beam employed, the linear relation between B and $\sec \theta$ might be

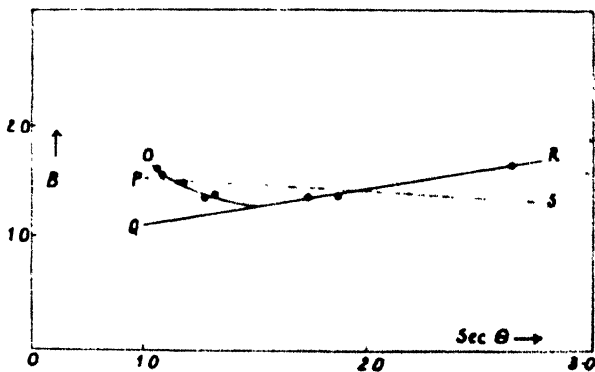


FIG. 8.

expected to hold. This was found to be the case with samples which could be readily centrifuged out of solution, however, with samples containing a large amount of gelatin, *i.e.*, those which centrifuged out with difficulty and those which required evaporation, this linear relation no longer held. The difference between the

two cases is no doubt due to the lowering of the specimen absorption on diluting the specimen; this is supported by the observation that it was often difficult to see the shadow cast by the specimen on the fluorescent screen in the camera with the latter class of specimens, while no such difficulty was observed with the former class. In addition, the exposure time for the latter class would decrease *always* 40 per cent. or so in order to produce satisfactory line densities. The central line broadening which is consistent with such a suggestion, may be seen in many of the reproductions in Part I, and also in Fig. 6 of this part. It will be observed that this is in every way identical with the diffraction diagram of the very transparent MgO (Fig. 1). The

effect of making it strongly absorbing is shown in Fig. 7, it is seen that although there is a slight reduction in the central line breadths, the effect is not as great as might be expected from a comparison of Figs. 1 and 2. This, however, is most probably due to the layer not being sufficiently thin.

The effect of this decrease in absorption on the $B/\sec. \theta$ graph is shown in Fig. 8: OR is a curve obtained from a sample containing excess gelatin, it is seen that the central line breadths are very large as in Fig. 6; QR represents the linear relation as would be expected from the form of the Scherrer equation and is that actually obtained from samples containing a small amount of gelatin; PS is the slope of the experimental curve OR as obtained by the direct application of least squares to the experimental line breadths, thus in this latter case the calculated particle sizes become either very large or even negative. Cameron² has reported a similar effect when using samples of low atomic weight, *i.e.*, of low absorbing properties. It was not considered justifiable, in view of the unsatisfactory state of affairs existing with regard to this equation, to calculate the particle sizes using the line breadths from the three major angles as is done, in similar circumstances, with the Brill method below.

Application of the Brill Method.

The unsatisfactory results obtained by the use of the Scherrer equation led to the employment of Brill's first modification of von Laue's theory. An account of this method has already been given.

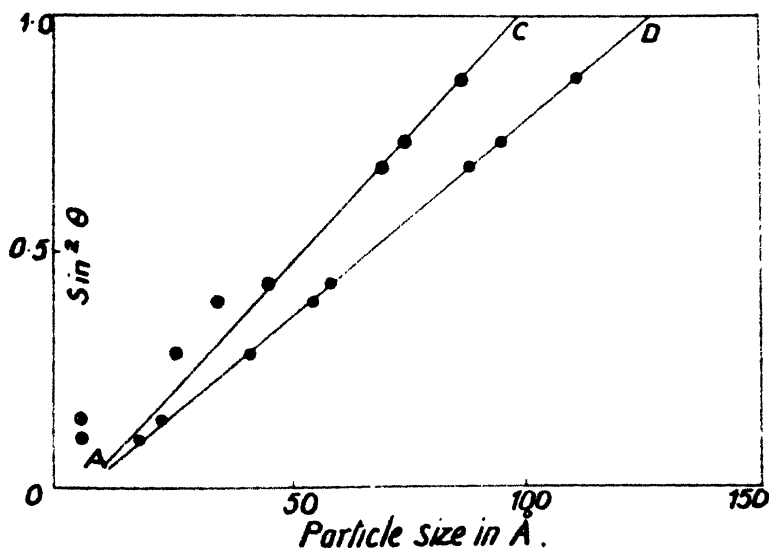


FIG. 9.

Two typical extrapolation graphs to find the particle size at $\sin^2 \theta = 1$ are shown in Fig. 9. The corresponding particle sizes being 98 Å. and 128 Å. respectively. The upper graph AC (98 Å.) is that obtained from a sample containing a large amount of gelatin; the effect of the central line broadening is again apparent as in Fig. 8, *i.e.*, the calculated particle sizes from these low angles are much lower than would be expected from the more reliable large angles. In the lower graph AD (128 Å.), the extrapolation, as would be expected, passes through all the points. In all cases the extrapolation was carried through the points obtained from the large angles (55° to 67°); the existence of these lines at large angles removes one of the main objections to the method.³

All the particle sizes for the experiments recorded in Part I. were obtained in this way. It was, on the whole, found entirely satisfactory in arranging the results in the correct order of magnitude without reference to the absolute values of the sizes.

Summary.

This paper deals with the experimental technique involved in the determination of the particle sizes of the various coagulates reported in Part I.

The Scherrer equation was found unsatisfactory for samples which had been diluted with gelatin, *i.e.*, when the sample was no longer strongly absorbing. This confirms the general conclusions of von Laue, Brill and Cameron.

The reported results were calculated from Brill's first modification of von Laue's theory, which was found satisfactory for placing the results in the correct order of size without reference to their absolute values.

The authors wish to express their thanks to Professor F. G. Donnan, C.B.E., F.R.S., for his interest in the work.

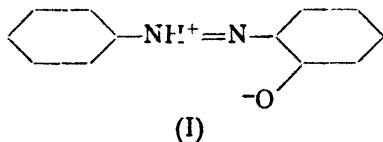
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DIPOLE MOMENT AND MOLECULAR STRUCTURE. PART XVII.* THE DIPOLE MOMENTS OF AZO-DYES AND SOME SIMILAR SUBSTANCES.

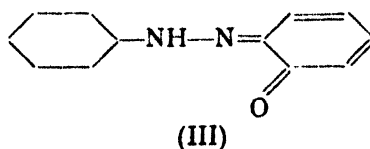
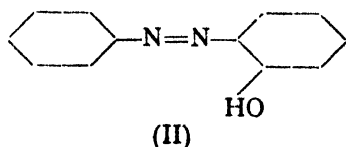
BY ERNST BERGMANN AND (MISS) ANNA WEIZMANN.

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The constitution of the amino- and *p*-hydroxy-azo-dyes seems quite settled, but that of the *o*-hydroxy-azo-compounds is still a matter of discussion. A new point of view has been introduced by R. Kuhn,¹ who proposed a Zwitter-ion structure (I),²



combining in itself to a certain extent both of the azoid (II) and quinoid (III) formulæ,



* Part XVI., *J. Chem. Soc.*, 1936, 402.

¹ *Naturwiss.*, 1932, 20, 619.

² Such formulæ had already been suggested by P. Blumberger, *Chem. Weekblad*, 1927, 24, 1.

The occurrence of such a form, even in small quantities, should be readily detectable, since its dipole moment should be abnormally high (about 20 D.). We have therefore determined the dipole moment of several azo-dyes (not only *ortho*-hydroxy-azo-dyes), both in order to compare their dipole moments and to determine the structure of *p*-hydroxy-azo- and amino-azo-compounds, in which the possibility of the same isomerism or tautomerism has never been excluded by decisive experiments (Table I.).

TABLE I*.

<i>c.</i>	ρ .	ϵ .	n^2 .	$P_{\frac{1}{2}}$.	$PE_{\frac{1}{2}}$.	P .	PE .	P_{A+0} .
<i>o</i>-Hydroxy-azobenzene.^a $t = 15.4^\circ$ C. Benzene.								
0	0.8841	2.2932	—	26.579	—	—	—	—
0.0111	0.8901	2.3342	—	27.435	—	103.98	calculated 69.35	34.6
0.0165	0.8930	2.3546	—	27.859	—	104.32		35.0
0.0219	0.8959	2.3766	—	28.306	—	105.40		36.0
0.0271	0.8988	2.3958	—	28.707	—	105.06		35.7
$P_{A+0}^\infty = 36.7$.				$\mu = 1.31$ D.				
<i>1</i>-Benzene-azo-2-naphthol.^b $t = 16.3^\circ$ C. Carbon disulphide.								
0	1.2691	2.6390	—	21.158	—	—	—	—
0.00742	1.2670	2.6781	—	21.875	—	117.80	calculated 76.59	41.2
0.01080	1.2661	2.6950	—	22.198	—	117.46		40.9
$P_{A+0}^\infty = 42$.				$\mu = 1.4$ D.				
<i>2</i>-Benzene-azo-1-naphthol.^c $t = 28.2^\circ$ C. Benzene.								
0	0.8688	2.2676	—	26.666	—	—	—	—
0.00591	0.8733	2.3017	—	27.376	—	146.78	calculated 78.9	67.9
0.01452	0.8799	2.3414	—	28.453	—	149.83		70.9
$P_{A+0}^\infty = 69.4$ (average).				$\mu = 1.8$ D.				
<i>p</i>-Amino-azobenzene.^d $t = 15.4^\circ$ C. Benzene.								
0	0.8841	2.2932	—	26.576	—	—	—	—
0.00805	0.8869	2.3877	—	28.211	—	229.57	calculated 71.249	158.2
0.01092	0.8880	2.4206	—	28.739	—	224.56		153.3
0.0152	0.8895	2.4709	—	29.573	—	223.80		152.5
$P_{A+0}^\infty = 156.8$.				$\mu = 2.71$ D.				

* The figures have the following significance: *c* molar fraction, ρ density, ϵ dielectric constant, n refractive index, $P_{\frac{1}{2}}$ total polarisation ($PE_{\frac{1}{2}}$ electronic polarisation) for the solution, $P(PE)$ the same for the solute, P_{A+0} atomic and orientation polarisation, which is extrapolated graphically to infinite dilution (P_{A+0}^∞).

For part of the substances we had at our disposal an Abbé refractometer; for the others the Zeiss interferometer, which which, however, it is not possible to determine the refractive index of highly coloured substances, at least not at the same concentrations as the dielectric constant. In these cases PE was calculated from the atomic and bond refractivities, or was determined at much lower concentrations, the average of the observed values being used in the case of high concentrations. This procedure is justified, since PE does not depend on the concentration.

^a Commercial preparation recrystallised until constant m.p. 83° .

^b Zincke and Rathgen, *Ber.*, 1886, 19, 2485. From alcohol; m.p. 133° .

^c Zincke, *Ber.*, 1883, 16, 1563; 1884, 17, 8030; m.p. 138° .

^d M.p. 126° .

TABLE I.—Continued.

c.	ρ .	ϵ .	n_D^2 .	P_H .	PE_H .	P.	PE .	$PA+0$.
4-Benzene-azo-1-naphthylamine.^e $t = 15.6^\circ$ C. Benzene.								
—	0.8835	2.2926	—	26.582	—	—	—	—→
0.00882	0.8903	2.3877	—	28.238	—	214.21	} calculated 76.59	137.6
0.01247	0.8931	2.4300	—	28.936	—	215.36		138.8
0.01598	0.8958	2.4693	—	29.616	—	216.41		139.8
$P_{A+0}^\infty = 140.$				$\mu = 2.56$ D.				
Dimethylamino-azobenzene.^f $t = 26.9^\circ$ C. Benzene.								
0	0.8704	2.2702	2.2372	26.656	26.171	—	—	—
0.00500	0.8732	2.3712	2.2479	28.287	26.491	348.74	89.36	254.3
0.00885	0.8754	2.4325	2.206	29.277	26.803	322.87	97.57	228.4
0.01264	0.8776	2.4929	2.2696	30.237	27.059	309.94	96.38	215.5
							(Average 94.44)	
$P_{A+0}^\infty = 279.$				$\mu = 3.68$ D.				
1-Benzene-azo-2-naphthylamine.^g $t = 15.8^\circ$ C. Benzene.								
0	0.8835	2.2924	—	26.582	—	—	—	—→
0.01058	0.8919	2.3724	—	28.078	—	167.95	} calculated 76.59	91.4
0.01413	0.8947	2.3985	—	28.565	—	166.92		90.3
0.1759	0.8975	2.4283	—	29.099	—	169.66		93.0
$P_{A+0}^\infty = 97.5.$				$\mu = 2.14$ D.				
α-Naphthylamine.^h $t = 22.8^\circ$ C. Benzene.								
0	0.8759	2.2783	2.2470	26.623	26.164	—	—	—→
0.02271	0.8841	2.3604	2.2680	28.045	26.706	89.21	50.08	39.1
0.03176	0.8876	2.3962	2.2750	28.646	26.911	90.32	49.38	40.9
0.04159	0.8914	2.4352	2.2892	29.295	27.210	90.86	51.33	39.5
0.05012	0.8948	2.4717	2.2986	29.820	27.435	90.41	51.53	38.9
$P_{A+0}^\infty = 43.4.$				$\mu = 1.44$ D.				
β-Naphthylamine.ⁱ $t = 22.8^\circ$ C. Benzene.								
0	0.8753	2.2783	2.2470	26.623	26.163	—	—	—→
0.02309	0.8826	2.3928	2.2692	28.561	26.780	110.56	52.88	57.7
0.02551	0.8833	2.3995	2.2710	28.687	26.836	107.52	52.55	55.0
0.03154	0.8852	2.4315	2.2795	29.211	27.037	108.68	53.80	54.8
$P_{A+0}^\infty = 63.0.$				$\mu = 1.74$ D.				
p-Hydroxy-azobenzene.^j $t = 14.7^\circ$ C. Benzene.								
0	0.8849	2.2947	—	26.573	—	—	calc.	—→
0.00503	0.8861	2.3176	—	27.071	—	125.59	69.35	56.2
$P_{A+0}^\infty = 56.24.$				$\mu = 1.62$ D.				

^e Griess, *Annalen*, 1866, **137**, 60. From 25 per cent. aqueous alcohol; m.p. 122° .

^f Moehlau, *Ber.*, 1884, **17**, 1491. From methyl alcohol; m.p. 117° .

^g 7. 1-Benzene-azo-2-naphthylamine. Bamberger and Schieffelin, *Ber.*, 1889, **22**, 1376; m.p. 102° .

^h Commercial sample, several times recrystallised.

ⁱ As ^h.

^j Oddo and Puxeddu, *Ber.*, 1905, **38**, 2755; m.p. 152° .

TABLE I.—Continued.

<i>c.</i>	<i>p.</i>	<i>ε.</i>	<i>n_D²⁰</i>	<i>P_D²⁰</i>	<i>P_E²⁰</i>	<i>P.</i>	<i>P_E</i>	<i>P_{A+0}</i>
<i>p</i>-Hydroxy-azobenzene.^k <i>t</i> = 15.2° C. Dioxane.								
0	1.0342	2.2369	—	24.841	—	—	—	→
0.01559	1.0390	2.3598	—	26.931	—	158.87	} calculated 69.35	89.5
0.02105	1.0406	2.4011	—	27.631	—	157.34		88.0
0.04073	1.0467	2.5579	—	30.200	—	156.41		87.1
$P_{A+0}^{\infty} = 89.0.$				$\mu = 2.04 \text{ D.}$				
4-Benzene-azo-1-naphthol.^l <i>t</i> = 28.3° C. Dioxane.								
0	1.0251	2.2317	2.0050	24.987	21.542	—	—	→
0.00373	1.0264	2.2645	2.0161	25.595	21.839	188.0	101.1	86.9
0.00573	1.0271	2.2875	2.0218	25.997	21.995	201.4	100.7	100.7
$P_{A+0}^{\infty} = 93.8 \text{ (average).}$				$\mu = 2.1 \text{ D.}$				
<i>p</i>-Methoxy-azobenzene.^m <i>t</i> = 22.8° C. Benzene.								
0	0.8753	2.2783	2.2377	26.623	26.025	—	—	—
0.01107	0.8800	2.3226	2.2560	27.621	26.652	116.82	82.73	34.1
0.01920	0.8835	2.3500	2.2741	28.374	27.185	117.83	86.40	31.4
0.02550	0.8862	2.3809	2.2840	28.960	27.537	118.26	85.33	32.9
0.03462	0.8900	2.4186	2.3043	29.809	28.135	118.64	86.98	31.7
$P_{A+0}^{\infty} = 34.8.$				$\mu = 1.29 \text{ D.}$				
4-Benzene-azo-1-methoxy-naphthalene.ⁿ <i>t</i> = 24.8° C. Benzene.								
0	0.8730	2.2743	2.2410	26.639	26.146	—	—	—
0.01346	0.8821	2.3267	2.2810	27.976	27.301	125.97	111.97	14.0
0.02165	0.8877	2.3656	2.3007	28.888	27.931	130.39	108.69	22.0
$P_{A+0}^{\infty} = 18.00 \text{ (average).}$				$\mu = 0.93 \text{ D.}$				
Benzophenone-hydrazone.^o <i>t</i> = 15.6° C. Benzene.								
0	0.8838	2.2928	2.2928	26.578	26.578	—	—	—
0.00093	0.8842	—	2.2938	—	26.617	—	69.43	—
0.00244	0.8847	—	2.2954	—	26.669	—	69.91	—
0.00277	0.8850	—	2.2958	—	26.699	—	70.22	—
0.01723	0.8909	2.4174	—	28.826	—	157.02	} 69.85	87.2
0.02076	0.8923	2.4427	—	29.279	—	156.67		86.8
0.02979	0.8960	2.5058	—	30.404	—	158.36		88.5
$P_{A+0}^{\infty} = 87.50.$				$\mu = 2.02 \text{ D.}$				
Benzophenone-phenylhydrazone.^p <i>t</i> = 15.3° C. Benzene.								
0	0.8842	2.2934	2.2934	26.575	26.575	—	—	→
0.00044	0.8845	—	2.2945	—	26.657	—	109.78	—
0.00032	0.8848	—	2.2958	—	26.754	—	110.87	—
0.00131	0.8855	—	2.2985	—	26.956	—	114.24	—
0.01124	0.8916	2.4049	—	28.685	—	214.249	} 111.63	102.6
0.01527	0.8943	2.4498	—	29.896	—	217.842		106.2
0.02591	0.9014	2.5521	—	31.406	—	213.027		102.0
$P_{A+0}^{\infty} = 106.00.$				$\mu = 2.22 \text{ D.}$				

^k Witt and Dedichen, *Ber.*, 1897, 30, 2657; m.p. 206°.^l M.p. 54°.^m Interaction between 4-benzene-azo-1-naphthol and diazomethane (Smith, *J. Chem. Soc.*, 1908, 93, 845); m.p. 82°.ⁿ Curtius, *J. prakt. Chem.*, 1891, 44, 194; m.p. 98°.^o Schlenk and Bergmann, *Annalen*, 1928, 463, 312; m.p. 137°.^p Goldschmidt and Schranzhofer, *Monatsh.*, 1895, 16, 808; m.p. 152°.

TABLE I.—*Continued.*

<i>c.</i>	<i>p.</i>	<i>e.</i>	<i>n_D²⁰</i>	<i>P_D²⁰</i>	<i>P_{E_D}²⁰</i>	<i>P.</i>	<i>P_E</i>	<i>P_{A+0}</i>
Fluorenone-phenylhydrazone.^a <i>t</i> = 16.0° C. Benzene.								
0	0.8834	2.2920	2.2920	26.579	26.579	—	—	—→
0.00029	0.8836	—	2.2923	—	26.590	—	64.38	—
0.00059	0.8839	—	2.2925	—	26.611	—	80.86	—
0.00071	0.8840	—	2.2927	—	26.619	—	82.32	—
0.00181	0.8848	—	2.2930	—	26.668	—	75.89	—
0.00950	0.8909	2.3606	—	27.954	—	171.36	(75.86)	95.5
0.01242	0.8930	2.3780	—	28.311	—	169.54		93.6
0.01457	0.8950	2.3969	—	28.082	—	170.78		94.9
$P_{A+0}^{\infty} = 98.0.$				$\mu = 2.12 \text{ D.}$				
2.3-Diphenylindone-phenylhydrazone.^r <i>t</i> = 14.2° C. Dioxane.								
0	1.0354	2.2373	—	24.818	—	—	—	—→
0.00856	1.0406	2.2998	—	26.270	—	194.39	} calcu- lated	77.5
0.01251	1.0430	2.3262	—	26.909	—	192.05		75.2
0.01803	1.0403	2.3637	—	27.813	—	190.98		74.1
$P_{A+0}^{\infty} = 81.5.$				$\mu = 1.93 \text{ D.}$				
Benzophenone-benzylphenylhydrazone.^s <i>t</i> = 25.9° C. Benzene.								
0	0.8738	2.2757	2.2371	26.632	26.662	—	—	—→
0.00933	0.8815	2.3785	2.2573	28.807	27.028	259.56	129.53	130.0
0.01264	0.8842	2.4040	2.2651	29.419	27.372	240.99	129.61	117.4
0.01899	0.8894	2.4659	2.2747	30.784	27.940	345.27	125.99	119.3
$P_{A+0}^{\infty} = 139.$				$\mu = 2.60 \text{ D.}$				
β-Naphthoquinone-β-benzyl-phenylhydrazone.^t <i>t</i> = 29.0° C. Benzene.								
0	0.8679	2.2660	2.2327	26.671	26.174	—	—	—→
0.00633	0.8748	2.3146	2.2437	27.734	26.681	194.7	106.3	88.4
0.00812	0.8768	2.3281	2.2476	28.037	26.837	194.9	107.9	87.0
$P_{A+0}^{\infty} \text{ (average)} = 87.7.$				$\mu = 2.2 \text{ D.}$				
Quinolein-yellow.^u <i>t</i> = 14.2° C. Dioxane.								
0	1.0360	2.2373	2.2373	24.803	24.803	—	—	—
0.00014	1.0362	—	2.2384	—	24.816	—	110.85	—
0.00030	1.0364	—	2.2400	—	24.836	—	135.00	—
0.00223	1.0390	2.2962	—	25.673	—	411.21	125.93	285.3
$P_{A+0}^{\infty} = 285.28.$				$\mu = 3.64 \text{ D.}$				

^a Schlenk and Bergmann, *Annalen*, 1928, **463**, 222; m.p. 179°.^r From benzophenone (4.6 g.) and benzylphenyl-hydrazine (5 g.) in acetic acid (20 c.c.) at boiling temperature for two hours. From alcohol; m.p. 110° (compare Bovini, *R.A.L.*, [3] 1913, **22**, II., 465).^s β -Naphtho-quinone (3.2 g.) in glacial acetic acid (25 c.c.) and benzyl-phenyl-hydrazine (4.0 g.) in conc. hydrochloric acid (3.3 c.c.) are mixed and left in the ice-chest for twenty-four hours. The dark violet product is filtered and crystallised from alcohol; m.p. 106°. (Found: C, 81.3; H, 6.1. Calc. for $C_{22}H_{16}ON_2$: C, 81.6; H, 5.3.)^t According to Jacobsen and Reimer, *Ber.*, 1884, **16**, 1082, as follows: phthalic anhydride (50 g.), quinaldine (50 g.), and zinc chloride (fused, 50 g.) are heated at 200° C. for two hours. The mass is warmed with concentrated sulphuric acid (200 c.c.) on the water-bath and poured into water (4 litres). The insoluble residuum is heated again with the acid (100 c.c.) and the mass poured into water (2 litres). The product is filtered, dried and recrystallised from a mixture of propyl and amyl alcohol. Cotton-wool-like needles, m.p. 240°. Yield 22 g.^u Commercial product, recrystallised from propyl alcohol; m.p. 172°.

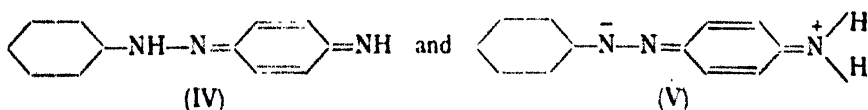
TABLE I.—Continued.

<i>c.</i>	<i>p.</i>	<i>a.</i>	<i>n^D.</i>	<i>P_D.</i>	<i>PE_D.</i>	<i>P.</i>	<i>PE.</i>	<i>P_A+0.</i>
Xanthone.^v <i>t</i> = 14.4° C. Benzene.								
0	0.8853	2.2964	2.2964	26.585	26.585	—	—	—→
0.00098	0.8860	—	2.2976	—	26.621	—	63.26	—
0.00197	0.8867	—	2.2988	—	26.641	—	63.37	—
0.00633	0.8898	2.3822	2.3044	27.914	26.819	236.39	63.47	173.0
0.01004	0.8925	2.4417	—	28.799	—	247.14	} average	183.8
0.01322	0.8948	2.4872	—	29.469	—	244.83		63.37
$P_{A+0}^{\infty} = 198.$				$\mu = 3.07 \text{ D.}$				
Xanthene.^w <i>t</i> = 28.0° C. Benzene.								
0	0.8691	2.2680	2.2314	26.664	26.119	—	—	—→
0.02313	0.8790	2.3448	2.2485	28.281	26.853	96.68	57.88	38.8
0.02535	0.8800	2.3554	2.2503	28.193	26.926	86.98	57.95	29.0
0.02938	0.8828	2.3542	2.2536	28.554	27.058	90.99	58.09	32.9
$P_{A+0}^{\infty} = 33.58 \text{ (average).}$				$\mu = 1.28 \text{ D.}$				
Azobenzene.^x <i>t</i> = 15.1° C. Dioxane.								
0	1.0344	2.2370	—	24.837	—	—	—	—→
0.04527	1.0378	2.2772	—	26.544	—	62.55	62.55	0
0.08932	1.0412	2.3093	—	28.130	—	61.71	61.71	0
$\mu = 0.$								

^v Heller and Kostanecki, *Ber.*, 1908, 41, 1325; m.p. 99°.

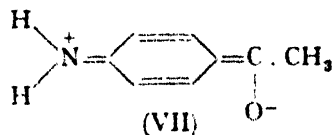
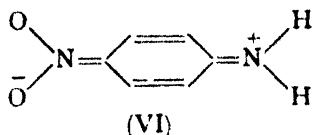
1. Zwitterion Formulæ.

Since the values for the *ortho*-hydroxy-azo-dyes are not abnormally high, we conclude that these substances cannot contain remarkable amounts of the Zwitterion-form in their solutions. Indeed, Kuhn himself has recently³ shown that 4-benzene-azo-1-naphthol does not raise the dielectric constant of its solvents, pyridine and nitrobenzene. It is very remarkable that the *p*-amino-azo compounds have anomalously high moments, as compared with the "normal" values of aniline 1.55,⁴ *N*-dimethylaniline 1.58,⁵ and α - and β -naphthylamine (see Table I.), the higher value for the β -isomer agreeing with earlier data.⁶ Obviously, *p*-amino-azo compounds should have the dipole moment of the group NR_2 , since such compounds as azo-benzene have zero moments.⁷ Here, again, two formulæ (IV) and (V) are possible:

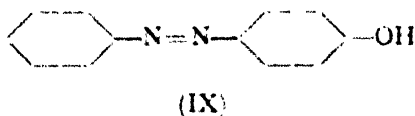
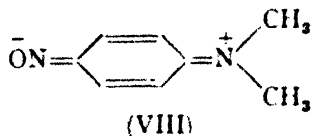
³ *Annalen*, 1935, 516, 143, 151, published some time after our preliminary publication, *Chemistry and Industry*, 1934, 54, 150.⁴ Hassel and Uhl, *Z. physik. Chem., B*, 1930, 8, 187.⁵ Fogelberg and Williams, *Physik. Z.*, 1931, 32, 27.⁶ Parts, *Z. physik. Chem., B*, 1930, 10, 264; Nakata, *Ber.*, 1931, 64, 2059.⁷ Bergmann, Engel and Sandor, *Ber.*, 1930, 63, 2572.

The more reasonable seems to be (V), since only that structure provides equally for the formation of amino- and dimethylamino-azo-benzene, without migration of an hydrogen atom,⁸ and seems to explain how, by addition of acid on the ends of the charged system, they form salts.

These particular "anomalous" compounds are not unique. The abnormally high dipole moment of *p*-nitraniline⁹ must certainly be accounted for by VI, since its N-dimethyl-derivative has a still higher



moment (6.87).¹⁰ It may be pointed out that the differences between the moments of amino- and N-dimethylamino-azo-benzene (0.97) and amino- and N-dimethyl-amino-nitrobenzene (0.72) are of the same order.^{10a} According to Hassel and Naeshagen,¹¹ *p*-amino-acetophenone has too high a moment. Here, too, the compound may exist partly in an excited form such as VII. The ability of the carbonyl group to be converted into a semipolar double bond system (VII) has been discussed by McKenzie and his co-workers.¹² Furthermore, as we have pointed out,³ the unusually high moment of nitroso-dimethylaniline may easily be explained



by VIII, which accords with its chemical properties (hydrolysis to dimethylamine and *p*-quinone-monoxime, interaction with methyl iodide and with benzoyl chloride). Other explanations might be given; for instance, one might assume mesomeric forms between the classical and our formulæ,¹³ or, what seems essentially the same, resonance between the two forms.¹⁴ Obviously, one cannot, by dipole moments alone, decide which is the most suitable.¹⁵ In the case of 1-benzene-azo-2-naphthylamine (the moment of which is not very different from that of 2-naphthylamine), one would accordingly assume that the proportion of Zwitterion molecules is somewhat small, or even zero, since the small difference between the two moments may easily be explained as due to an "ortho-effect" of the double bond on the C—OH— moment.^{15a}

⁸ For similar observations see Burawoy, *Ber.*, 1931, 64, 462, 479.

⁹ *Trans. Faraday Soc.*, 1934, 30, lxxii; and Porter and Kumler, *J. Am. Chem. Soc.*, 1934, 56, 2549.

¹⁰ Marsden, *ibid.*, p. lxxiii. Compare Marsden and Sutton, *J. Chem. Soc.*, 1936, 599.

^{10a} Compare the moment of *p*-nitro-phenylhydrazine (7.2 D); Ullrich, *Ber.*, 1935, 68, 1677.

¹¹ *Z. physikal. Chem., B*, 1932, 18, 417.

¹² *Biochem. Z.*, 1929, 208, 456, 471.

¹³ Le Fèvre and Smith, *J. Chem. Soc.*, 1932, 2239.

¹⁴ Sutton, *Trans. Faraday Soc.*, 1934, 789.

¹⁵ Compare Arndt, *Ber.*, 1930, 63, 587, 2963, 3125.

^{15a} See the following paper.

2. Structure of *p*-hydroxy-azo-dyes.

Zwitterion formulæ for the *p*-hydroxy-azo-dyes are ruled out by their relatively low dipole moments. It remains to decide whether the dyes are quinoid or azoid compounds, and whether, indeed, an uniform formulation is possible. The dipole moment of *p*-hydroxy-azo-benzene in benzene solution is the same as that of phenol,¹⁶ so that its structure (IX) seems unambiguous, its moment being exclusively determined by that of the hydroxyl group. Again, *p*-methoxy-azo-benzene has a moment nearly identical with that of anisole.¹⁷ As a matter of fact, *p*-hydroxy- and *p*-methoxy-azo-benzene have in benzene solution identical absorption.¹⁸

Whilst the dipole moment of 4-benzene-azo-1-methoxy-naphthalene is sufficiently near to that of the methoxy-group in anisole to give a clue to the formulated structure, it is difficult to see why the corresponding hydroxy-compound and *p*-hydroxy-azobenzene have a somewhat high moment in dioxane solution, especially since azo-benzene itself has nearly the same total polarisation (which in this case is identical with the electronic polarisation) in benzene and dioxane. The change must therefore be structural, involving a partial (tautomeric) change into a quinoid hydrazone structure.¹⁹



3. Structure of *ortho*-hydroxy-azo-dyes.

For *o*-hydroxy-azobenzene and 1-benzene-azo-2-naphthol, the dipole values are those of the hydroxyl group; an azoid structure, in the solutions we have used, would be at variance with the spectroscopic findings of Burawoy and Markowitsch,²⁰ who state that all the *o*-hydroxy-azo compounds are quinone-hydrazones. Kuhn and Baer,¹⁸ however, on spectroscopic grounds, assume the azoid structure for *o*-hydroxy-azobenzene (similarity between the *o*- and *m*-hydroxy-azo-benzene bands), but a quinoid formula for 1-benzene-azo-2-naphthol. Since the influence of a possible chelation^{20a} cannot be evaluated, the dipole moments in the two above cases do not lead to any decision. On the other hand, our measurements with 2-benzene-azo-1-naphthol seem to agree with the spectroscopic findings and to show that the substance has (quinoid) hydrazone structure, because the difference between the dipole moments of the azo-dye and of the (certainly quinoid) β -naphthoquinone-benzyl-phenylhydrazone is no greater than that between the moments of benzophenone-phenylhydrazone and -benzylphenylhydrazone.

¹⁶ Donle and Gehrkens, 1.01 ± 0.03 ; *Z. physik. Chem.*, B, 1922, 18, 316.

¹⁷ Donle and Volkert, 1.23; *Z. physik. Chem.*, B, 1930, 8, 60.

¹⁸ Kuhn and Baer, *Annalen*, 1935, 516, 155.

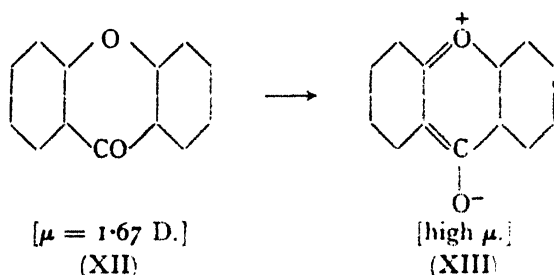
¹⁹ The various hydrazones we have investigated have dipole moments of the same magnitude as those under discussion; the dipole moment to be expected for (XI) cannot, of course, be calculated theoretically from the dipole moments of, say, benzophenone-phenylhydrazone and the carbonyl group, since the hydrazone group has no axial symmetry. Kuhn and Baer¹⁸ recently observed spectroscopically such a structural shift under the influence of solvents, even in the case of 4-benzene-azo-1-naphthol. (The possibility of tautomerism of *p*-hydroxy-azo-compounds has been mentioned by Borsche, Mueller and Bodenstein, *Annalen*, 1929, 472, 20; in a certain number of such substances Lauer and Miller (*J. Am. Chem. Soc.*, 1935, 57, 520) have proved a quinonoid activity.)

²⁰ *Annalen*, 1933, 503, 197; 1933, 504, 60.

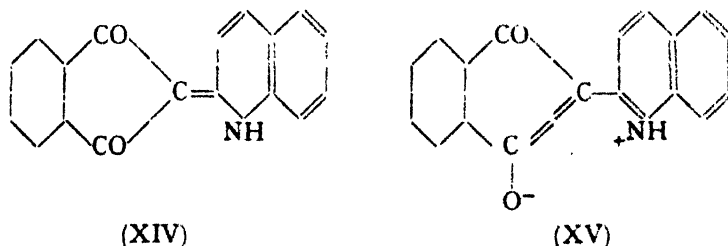
^{20a} Compare Blumberger, *Chem. Centralbl.*, 1935, I, 3273.

4.

Measurements of dipole moments may, as a rule, be used for detecting substances of the Zwitterion type, since these should exhibit an unusually high electric moment. As a matter of fact, the method has been used qualitatively for amino-acids and peptides,²¹ and also for other organic molecules.²² Two new cases, xanthone and quinoleine yellow are here discussed. The dipole moment of xanthone should be equal to the difference between those of the carbonyl group²³ and of xanthene, the moment of which is due exclusively to the diphenyl ether system, participating in the ring—the assumption being made that the xanthene system is plane. The moment (1.28) for xanthene agrees reasonably with that of diphenyl ether.²⁴ The "normal" moment of xanthone should be therefore $2.95 - 1.28 = 1.67$ D, whilst that observed is as high as 3.07. The unusually low chemical activity of xanthone agrees with the conclusion that the moment is due to the fact that part of the xanthone molecules exist in a Zwitterion state (XIII).²⁵



For quinoleine yellow, a Zwitterion formula (XV) was once suggested by R. Kuhn,²⁶ instead of the "unexcited" formula (XIV), and now withdrawn.²⁷ Our measurements confirm this; the value of 3.64 for the



dipole moment in dioxane solution is not low but, since quinoleine²⁸ itself has a moment of 2.14, only a small fraction of the molecule can exist in Zwitterion form.

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²¹ W. Kuhn and Martin, *Ber.*, 1934, **67**, 1526; *Z. physik. Chem., A*, 1936, **175**, 1; Devoto, *Z. physiol. Chem.*, 1933, **222**, 127, and earlier publications; R. Kuhn and Giral, *Ber.*, 1935, **55**, 908; *Naturwiss.*, 1935, **23**, 639.

²² Hunter and Partington, *J. Chem. Soc.*, 1933, 87, and Arndt, Martin and Partington, *ibid.*, 1935, 602; Le Fèvre, *J. Chem. Soc.*, 1936, 398; see also Sutton,¹⁸ and the authors.⁹

²³ Benzophenone, Bergmann, Engel and Meyer, *Ber.*, 1932, **65**, 446; 2.95.

²⁴ Bergmann and Tschudnowsky, *Z. physik. Chem., B*, 1912, **17**, 107; 1.13.

²⁵ Collip, *J. Chem. Soc.*, 1904, **85**, 973, suggested a similar formula for pyrones.

²⁶ *Naturwiss.*, 1932, **20**, 618.

²⁷ Kuhn and Baer, *Annalen*, 1935, **516**, 155.

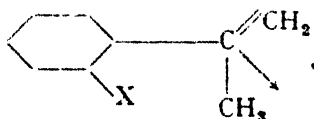
DIPOLE MOMENT AND MOLECULAR STRUCTURE. PART XVIII. THE DIPOLE MOMENTS OF SUBSTITUTED α -METHYL-STYRENES.

BY ERNST BERGMANN AND (MISS) A. WEIZMANN.

Received 14th April, 1936.

Ortho-disubstituted benzenes have anomalous dipole moments, differing from the vectorial sum of the single group-moments. One may explain the "ortho-effect," by assuming either that the group moments remain constant, there being a widening of the angle of the substituent valencies owing to the "volume" of the substituents,¹ or that the group moments change by mutual induction, whilst the direction of the ring-substituent bonds remains constant²; or, again, both effects may apply at the same time.

That *widening of the angle* between *ortho*-substituents occurs to a certain extent, has since been demonstrated.³ In order to ascertain the magnitude of the *induction effects* concerned, we have studied in benzene solution the dipole moments of several *ortho*-substituted α -methylstyrenes: since the



ethylenic group, having no marked dipole moment, is highly polarisable. In view of the smallness of the carbon atoms, it is unlikely that X is deflected from its normal direction.⁴ The theoretical dipole moment of the *ortho*-substituted α -methylstyrenes should be equal to the sum of the moment of X and the resultant moment of the unsaturated system. The latter should be about 0.5 and parallel to the moment of the nucleus-X bond, since it results from the styrene moment,⁵ and the methyl moment, the angle between the C-methyl and the C-phenyl bond being assumed to be 120° .⁶ Induction would, as usual, tend to decrease the expected moment of (X + 0.5).

Table I. shows that there is a marked influence, except in the first case, where the theoretical moment has actually been found; *o*-xylene, however, also has the theoretical moment.⁷ In α -naphthyl-methyl-ethylene, already, the expected moment has fallen to zero. Comparing

¹ Suggested originally by Bergmann, Engel and Sandor, *Z. physik. Chem. B*, 1930, 10, 106, as a working hypothesis which proved quite satisfactory (compare Hassel and Naeshagen, *ibid.*, 1931, 12, 79).

² K. F. Herzfeld and Smallwood, *J. Am. Chem. Soc.*, 1930, 52, 1919.

³ Hendricks, Maxwell, Mosley and Jefferson, *J. Chem. Physics*, 1933, 1, 542; and de Lazzio, *Trans. Faraday Soc.*, 1934, 30, 892.

⁴ Compare Adams and co-workers, *J. Am. Chem. Soc.*, 1928, 50, 2498; 1930, 52, 2859.

⁵ See Sutton, *Trans. Faraday Soc.*, 1934, 30, 798.

⁶ According to Brockway, Beach and Pauling, *J. Am. Chem. Soc.*, 1935, 57, 2684: $116 \pm 2^\circ$.

⁷ See *inter alia*, Tiganik, *Z. physik. Chem., B*, 1931, 13, 425.

TABLE I.

Compound.	Dipole Moment (Benzene Solution).	Group Moment of X.
α -Dimethylstyrene	0.8	0.4
α -Naphthyl-methyl-ethylene	0	0
<i>o</i> -Methoxy- α -methylstyrene	1.48	1.23
<i>o</i> -Fluoro- α -methylstyrene	1.54	1.45
<i>o</i> -Bromo- α -methylstyrene	1.87	1.49
<i>o</i> -Iodo- α -methylstyrene	1.48	1.30
<i>m</i> -Methoxy- α -methylstyrene	1.65	1.23
<i>m</i> -Chloro- α -methylstyrene	1.80	1.56
<i>p</i> -Methoxy- α -methylstyrene	1.33	1.23
<i>p</i> -Bromo- α -methylstyrene	1.45	1.49

the moments of *o*-methoxy-, *o*-fluoro-, *o*-bromo- and *o*-iodo- α -methylstyrene, the lowering effect is seen to be great in the case of the methoxy-, fluoro- and iodo-compound, and relatively small with the bromo-derivative.

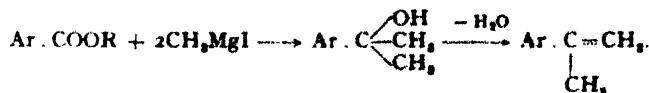
For purposes of comparison, we have also investigated some *m*- and *p*-substituted α -methyl-styrenes. It should be possible to calculate their moments from those of X by vectorial addition of 0.5 D. at angles of 60° or 120° respectively. The theoretical value for *m*-chloro- α -methylstyrene is 1.86, for the *p*-bromo-compound 1.32, both in good agreement with the observed figures. For the methoxy-compounds no exact calculation is possible due to the spatial structure of the oxygen valencies, but the observed values show the expected magnitude. These data, however, support the dipole moment ascribed above to the unsaturated system of α -methylstyrene, and show that the deviations discussed are really due to an inductive effect.

TABLE II.*

<i>c</i> .	<i>p</i> .	<i>a</i> .	π^2 .	P_1 .	P_{H_1} .	<i>P</i> .	P_E .	P_{A+0} .
<i>o</i> -, α -Dimethylstyrene. ^a <i>t</i> = 25.8° C.								
0	0.8730	2.2759	2.2344	26.632	26.016	—	—	—
0.04349	0.8739	2.3200	2.2380	28.108	26.859	60.57	45.35	15.2
0.07060	0.8738	2.3415	2.2393	28.929	27.371	59.17	45.18	14.0
$P_{A+0}^\infty = 16.0$.				$\mu = 0.8$ D.				

* For the significance of the figures, see page 1319.

^a All the materials were prepared as follows :



The dehydration of the carbinols which, owing to their inclination to spontaneous dehydration, could not always be isolated in an analytically pure form, was effected by heating with acetic anhydride, following the procedure of Staudinger and Breusch (*Ber.*, 1929, 62, 442).

o-Tolyl-dimethyl-carbinol was prepared from magnesium (3.9 gr.), methyl iodide (24 g.) and methyl *o*-toluate (11 g.); b.p. 80°/2 mm. Yield 9.5 g. The *o*, α -dimethylstyrene prepared from that carbinol with acetic anhydride (10 gr.) had b.p. 59-62°/11 mm.; $n_D^{20} = 1.5112$ (Kay and Perkin, *J. Chem. Soc.*, 1905, 87, 1083; Tiffenau, *Annales*, [8], 1907, 10, 194; Sabatier and Murat, *Compt. rend.*, 1913, 186, 185, *Annales*, [9], 1915, 4, 273).

TABLE II.—Continued.

c.	p.	c.	n _D ²⁰	P ₁	P ₂	P.	P _B	P _{A+0}
α-Naphthylmethyl-ethylene. ^b t = 26.7° C.								
o	0.8706	2.2706	2.2347	26.655	26.122	—	—	→
0.03889	0.8792	2.3003	2.2596	28.030	27.412	62.01	59.27	2.7
0.07277	0.8866	2.3217	2.2816	29.164	28.544	61.14	59.53	1.6
P _{A+0} [∞] = 2.17.				μ ~ 0 D.				
o-Methoxy-α-methylstyrene. ^c t = 26.9° C.								
o	0.8704	2.2702	2.2363	26.656	26.153	—	—	→
0.01651	0.8728	2.3184	2.2377	27.689	26.489	89.19	46.50	42.7
0.02468	0.8740	2.3489	2.2396	28.293	26.671	92.99	47.15	45.8
0.03682	0.8758	2.3804	2.2413	28.990	26.925	90.10	47.12	43.0
0.05339	0.8783	2.4281	2.2440	30.014	27.279	89.46	47.24	42.2
P _{A+0} [∞] = 45.0.				μ = 1.48 D.				
o-Fluoro-α-Methylstyrene. ^d t = 25.9° C.								
o	0.8738	2.2757	2.2344	26.632	26.022	—	—	→
0.02547	0.8787	2.3647	2.2347	28.189	26.288	87.76	36.50	48.0
0.03577	0.8806	2.3945	2.2506	28.725	26.633	86.49	43.11	46.7
							Average 39.80	
P _{A+0} [∞] = 49.0.				μ = 1.54 D.				
o-Bromo-α-methylstyrene. ^e t = 27.3° C.								
o	0.8710	2.2694	2.2363	26.626	26.135	—	—	→
0.01400	0.8813	2.3353	2.2366	27.844	26.386	113.62	44.12	69.5
0.01638	0.8830	2.3481	2.2380	28.074	26.448	114.86	45.27	69.6
0.02210	0.8872	2.3745	2.2386	28.555	26.557	113.91	45.24	68.7
P _{A+0} [∞] = 71.5.				μ = 1.87 D.				

^b Grignard, *Bull. Soc. Chim. France*, 1901, 25, 498; *Annales*, [7], 1901, 24, 472. B.p. 125°/8 mm.

^c The reaction of ethyl *o*-methoxy-benzoate (b.p. 138–144°/28 mm.) (18 g.) with magnesium (5.3 g.) and methyl iodide (37 g.) gave a mixture of the carbinol and the corresponding styrene derivative, boiling at 55–65°/1 mm. Therefore the product (10 gr.) was heated with the same quantity of acetic anhydride for 8 hours. B.p. 56–60°/1 mm.; yield 4.8 g. $n_D^{20} = 1.5296$. (Found: C, 80.8; H, 8.1; $C_{10}H_{11}O$ requires C, 81.1; H, 8.1.) It has already been reported by Béhal and Tiffeneau (*Compt. rend.*, 1904, 139, 140; *Bull. Soc. Chim. France* [4] 1908, 3, 315) that the above Grignard reaction gives immediately the unsaturated compound (compare Auwers, *Annalen*, 1917, 413, 303).

^d *o*-Fluoro-phenyl-dimethyl-carbinol, prepared in the usual manner, had b.p. 102–104°/20 mm.; analysis of this substance, as well as that of the corresponding ethylenic compound gave unsatisfactory figures for carbon, obviously due to the fluorine content. (Found: C, 68.7; H, 7.1. Calc. for $C_{10}H_{11}OF$: C, 70.0; H, 7.1.) For dehydration it was necessary to heat the carbinol (7.5 g.) with acetic anhydride (12 g.) for 8 hours. The styrene boiled at 62°/28 mm., and showed $n_D^{20} = 1.5009$. (Found: C, 77.2; H, 6.7; Calc. for C_9H_8F : C, 80.0; H, 6.7.)

^e From ethyl *o*-bromo-benzoate (28 g.), magnesium (6.2 g.) and methyl iodide (36.1 g.) (*o*-bromo-phenyl)-dimethyl-carbinol (13 g.) were obtained; b.p. 87–93°/1 mm. (Found: C, 51.0; H, 5.4. Calc. for $C_{10}H_{11}OBr$: C, 50.2; H, 5.1.) The treatment with acetic anhydride, even after twenty-four hours, was unsuccessful; on heating the carbinol with acetic anhydride in presence of a few drops of concentrated sulphuric acid, 4 gr. of the desired styrene derivative were obtained, boiling at 55–65°/0.9 mm.; $n_D^{20} = 1.5530$, which gave satisfactory analytical figures. (Found: C, 54.8; H, 4.9. Calc. for C_9H_8Br : C, 54.8; H, 4.6.)

TABLE II.—Continued.

<i>c.</i>	<i>p.</i>	<i>e.</i>	<i>n_D²⁰</i>	<i>P_T</i>	<i>P_{K_T}</i>	<i>P.</i>	<i>P_E</i>	<i>P_{A+0}</i>
<i>o</i>-Iodo-α-methylstyrene.[†] <i>t</i> = 26.1° C.								
0	0.8713	2.2718	2.2380	26.651	26.149	—	—	—→
0.01988	0.8935	2.3364	2.2482	28.041	26.734	96.60	55.58	41.0
0.02879	0.9035	2.3723	—	28.757	—	99.84	—	44.2
0.03010	0.9049	2.3779	2.2560	28.867	27.067	100.28	56.64	44.6
0.03825	0.9140	2.4026	2.2570	29.401	27.250	98.54	54.66	42.9
							Average	
							55.63	
$P_{A+0}^{\infty} = 45.0.$				$\mu = 1.48$ D.				
<i>m</i>-Methoxy-α-methylstyrene.[‡] <i>t</i> = 23.8° C.								
0	0.8742	2.2763	2.2347	26.630	26.012	—	—	—→
0.02039	0.8765	2.3401	2.2390	27.981	26.487	92.88	49.34	43.5
0.02440	0.8769	2.3474	2.2422	28.171	26.615	89.78	50.74	39.0
0.03295	0.8779	2.3561	2.2420	28.472	26.782	82.54	49.40	33.1
0.04675	0.8795	2.4025	2.2467	29.439	27.129	86.72	49.91	36.8
$P_{A+0}^{\infty} = 56.5.$				$\mu = 1.65$ D.				
<i>m</i>-Chloro-α-methylstyrene.[§] <i>t</i> = 26.5° C.								
0	0.8708	2.2710	2.2371	26.654	26.151	—	—	—→
0.01693	0.8763	2.3619	2.2434	28.240	26.502	120.35	46.94	73.4
0.02448	0.8788	2.3938	2.2437	28.814	26.621	114.91	45.15	69.8
0.03956	0.8837	2.4666	2.2470	30.077	26.897	113.20	45.02	68.2
$P_{A+0}^{\infty} = 74.0.$				$\mu = 1.89$ D.				
<i>p</i>-Methoxy-α-methylstyrene.[†] <i>t</i> = 25.7° C.								
0	0.8719	2.2725	2.2358	26.645	26.100	—	—	—→
0.00741	0.8727	2.2889	2.2371	27.039	26.271	79.93	49.13	30.8
0.01850	0.8738	2.3224	2.2404	27.763	26.545	87.10	50.15	36.7
0.03089	0.8751	2.3555	2.2440	28.507	26.850	86.94	50.38	36.6
0.03947	0.8760	2.3740	2.2470	28.961	27.070	85.24	50.68	34.9
							Average	
							50.37	
$P_{A+0}^{\infty} = 36.50.$				$\mu = 1.39$ D.				

[†] From methyl *o*-iodo-benzoate (52 g.), magnesium (10.4 g.) and methyl iodide (64 g.) the crude carbinol (40 gr.) was obtained; by repeated distillation *in vacuo*, 21 g. of a nearly pure product were obtained; b.p. 108–110°/0.9 mm. (Found: C, 42.2; H, 4.3; I, 4.3. Calc. for C₉H₉OI: C, 41.2; H, 4.2.) The carbinol was heated with the same amount of acetic anhydride for eight hours. Fractional distillation gave the styrene derivative (8.5 g.); b.p. 65–70°/0.9 mm.; $n_D^{20} = 1.5955$. (Found: C, 44.6; H, 3.9. Calc. for C₉H₉I: C, 44.3; H, 3.7.)

[‡] Béhal and Tiffeneau⁶ (cf. Auwers⁶). B.p. 110°/22 mm.; $n_D^{20} = 1.5399$.

[§] The carbinol, prepared from methyl *m*-chloro-benzoate, had b.p. 124–126°/18 mm. (Found: C, 63.1; H, 6.3; Cl, 6.2. Calc. for C₉H₉OCl: C, 63.5; H, 6.5.) Dehydration occurs if the carbinol (11 gr.) is heated with acetic anhydride (14 g.) for forty-eight hours. B.p. 105–108°/26 mm. (Found: C, 71.9; H, 6.6. Calc. for C₉H₉Cl: C, 71.1; H, 6.0.)

[†] B.p. 114°/20 mm. Compare Béhal and Tiffeneau.⁶

TABLE II.—Continued.

<i>c.</i>	<i>p.</i>	<i>a.</i>	<i>n_D²⁰</i>	<i>P_D²⁰</i>	<i>P_B²⁰</i>	<i>P_a</i>	<i>P_B</i>	<i>P_{A+0}</i>
<i>p</i> -Bromo- α -methylstyrene, ¹ <i>t</i> = 22.3° C.								
0	0.8759	2.2793	2.2414	26.621	26.057	—	—	—
0.01498	0.8855	2.3185	2.2485	27.508	26.476	85.82	54.07	31.7
0.02172	0.8899	2.3504	2.2509	28.111	26.649	95.22	53.25	42.0
0.02770	0.8936	2.3963	2.2530	28.895	26.803	108.73	52.34	56.4
0.03503	0.8984	2.4039	2.2560	29.156	26.991	99.00	52.74	46.3
$P_{A+0}^{\infty} = 44.09$ (Average).				$\mu = 1.45$ D.				

¹ Interaction between acetone (17 g.), magnesium (7 gr.) and *p*-dibromobenzene (59 g.) (Bergmann, *Ber.*, 1931, 64, 1481) gave the carbinol (44 g.) which could not be purified and therefore was heated with acetic anhydride (50 g.) for eight hours. The unsaturated product boiled at 58–60°/1.8 mm.; $n_D^{27} = 1.5778$. (Found : Br, 40.5 ; 40.3. Calc. for C_9H_7Br : Br = 40.6.)

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THE PHOTO REDUCTION OF FLUORESCENT SUBSTANCES BY VISIBLE LIGHT.

BY JOSEPH WEISS.

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Photo-reduction has been used for preparative purposes in the well-known investigations of Ciamician and Silber¹ to reduce various ketones in the presence of alcohols which are themselves oxidised to the corresponding aldehydes. According to a recent theoretical discussion,² this implies that the fluorescence of the ketones in the near ultraviolet is quenched by alcohols.

Many fluorescent substances which absorb in the visible region can similarly be reduced by the action of (visible) light in the presence of inorganic reducing substances which quench the fluorescence. Some of these reactions have been discussed already in connection with the quenching effect,³ but it should be pointed out that they can also be used for preparative purposes. The photoreduction of various fluorescent dyestuffs has been studied in detail.³

The reduction is carried out by irradiating a constantly stirred aqueous solution of the dyestuff containing $FeSO_4$ (about 1 molar) with the light of a powerful carbon arc with the exclusion of oxygen. The reaction, if made in neutral solution so that the ferric salt formed is hydrolysed and precipitated (as the basic salt), results in a quantitative reduction to the leuco-dye. By this method the following dyestuffs were readily reduced : methylene blue, thionine, brilliant-cresyl blue, eosin, uranine.

With a slight adjustment of the conditions the present method could obviously be applied to the reduction of various substances, but is practically confined to fluorescent compounds. The method has the advantage that the hydrogenation can be carried out at a low temperature and in practically neutral solution.

¹ *Ber.*, 1903, 36, 1575 ; 1910, 43, 945 ; 1907, 40, 2415 ; 1911, 44, 1280.

² J. Weiss and H. Fishgold, *Z. physik. Chem., B*, 1936, 32, 135.

³ J. Weiss, *Nature*, 1935, 136, 794.

The essential processes can be described by the following scheme :

[F* fluorescent substance]

(a) light absorption $F + h\nu \rightarrow F^*$ (excited molecule)

(b) fluorescence
(emission) $F^* \rightarrow F + h\nu$

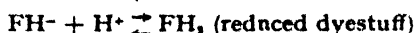
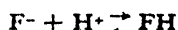
(c) photo-reduction $F^* + Fe^{++} \rightarrow F^- + Fe^{+++}$;
(quenching)

(d) re-oxidation $F^- + Fe^{+++} \rightarrow F + Fe^{++}$

In the case of a two-step reduction, we have the

(e) semiquinone equilibrium : $2F^- \rightleftharpoons F + F^-$.

and finally the electrolytic dissociation equilibria :



In acid solution where the Fe^{+++} ions formed in reaction (c) are not precipitated, when the irradiation ceases these dissolved Fe^{+++} re-oxidise the leuco-dye formed during illumination [reaction (d)], and the colour re-appears. In this case we have a rapidly established photochemical oxidation-reduction equilibrium.

This effect can very easily be made visible (in the absence of oxygen) by irradiating a solution containing the fluorescent dyestuff thionine ($\sim 10^{-5}$ molar) $FeSO_4$ ($\sim \frac{1}{2}$ molar) and H_2SO_4 ($\sim \frac{1}{10}$ molar) looking through a layer of the solution not less than 30 mm. thick.

Similar effects were described recently by v. Euler, Brandt and Hellström,⁴ working with the system methylen blue—ethyl alcohol—ferrous salt, and by Weber.⁵

From the theoretical discussion¹ it follows that the amount of photo-reduction increases with increasing light intensity, and that a high concentration of the reducing agent and a long (natural) lifetime of the excited state of the fluorescent substance are favourable. The reaction is naturally not confined to ferrous salts, but may also be carried out with other reducing substances, such as sulphites and sulphides.⁶

In principle, every fluorescent substance can be reduced by the influence of light, in the presence of suitable reducing substances, reversibly or irreversibly. This photo-reduction is identical with the elementary process of quenching of fluorescence. The dyestuff molecule in the excited state (F^*), which possesses² an unoccupied electronic level (due to the excitation of one electron to a higher level) can take up an electron from a reducing (quenching) substance into this level (according to reaction c). In this way the excitation energy in effect increases the electron-affinity of the dyestuff molecule (F).

The importance of the photo-reduction by ferrous ions for the assimilation process of green plants (photo-reduction of carbon dioxide with the help of the dyestuff chlorophyll under the influence of sunlight) has been discussed previously,³ and will be dealt with in detail in a paper to be published shortly in the *Journal of General Physiology*.

In conclusion I would like to thank Professor F. G. Donnan, F.R.S., for his continuous help and encouragement.

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¹ *Naturwiss.*, 1935, 23, 794.

² *Ibid.*, 486.

³ Cf. J. Weiss, *ibid.*, 610; J. Weiss and H. Fishgold, *Nature*, 1936, 137, 71.

FURTHER CONSIDERATIONS ON THE THERMODYNAMICS OF CHEMICAL EQUILIBRIA AND REACTION RATES.

BY M. G. EVANS AND M. POLANYI.

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1. Linear Relationships between Chemical Free Energies.

In a previous communication¹ we have stated for the reaction velocity constant (k)

$$k = \frac{1}{2} K v \quad . \quad . \quad . \quad (1)$$

where K is the equilibrium constant of the transition state and v the thermal velocity of the representative point along the reaction co-ordinate.² Since variations in v are small we can interpret the general empirical relationship.³

$$\log k = \alpha \log K + \text{const.} \quad . \quad . \quad . \quad (2)$$

as relating to K instead of k

$$\log K = \alpha \log K + \text{const.} \quad . \quad . \quad . \quad (3)$$

Thus, equations of the type (2) are seen to be relationships between the free energy changes of chemically analogous reactions one of them being an ordinary reaction, the other being represented by the passing of the system into the transition state. $RT \log K$ is the free energy change of the former, $RT \log K$ that of the latter reaction.

As might be expected from this point of view, relationships of the type (2) and (3) exist also between ordinary equilibrium constants of chemically analogous reactions. Evidence of this will be adduced in the present paper.

Looking, as we do, upon all these linear relationships as laws obtaining between the free energies of chemical reactions, we will try to give them a common explanation and, at the same time, will show that they can be further generalised and amplified.⁴

¹ *Trans. Faraday Soc.*, 1935, 31, 875.

² For a similar equation see H. Eyring, *J. Chem. Physics*, 1935, 3, 107, and Wynne-Jones and Eyring, *J. Chem. Physics*, 1935, 3, 492. Such equations represent generalisations of the transition state method in the form given by Wigner and Pelzer (*Z. physik. Chem., B*, 1932, 15, 445).

³ The best known examples of this relationship have been found by Brønsted (see *Chem. Rev.*, 1928, 5, 231) for the dissociation constants of acids and bases and their catalytic activities. The origins of this discovery go back to Snethlage (*Z. Elektrochem.*, 1912, 18, 539) who first showed the parallelism between acid strength and catalytic action of acid molecules and to H. S. Taylor (*Z. Elektrochem.*, 1914, 20, 201) who first related them quantitatively. More recently it has been recognised that Brønsted's law is an example of numerous relationships of the type 2 (see A. Frumkin, *Z. physik. Chem., A*, 1932, 160, 116; Hammett *Chem. Rev.*, 1935, 17, 125, and the later part of this paper).

⁴ A preliminary notice of the following considerations was published in *Nature*, 1936, 137, 530.

2. Thermodynamics of the Transition State. Molecular Fields.

The well-known laws of the thermodynamics of chemical reactions are :—

The mass action law

$$\log K = \sum_j \nu_j \log c_j - \sum_i \nu_i \log c_i \quad (4)$$

where the i 's constitute state 1 and the j 's state 2 of the reaction.

The reaction isochor

$$\left(\frac{\partial \log K}{\partial T} \right) = \frac{H_p}{RT^2} \quad (5)$$

where H_p (the heat of reaction) $= \sum_j \nu_j (\epsilon_j + p\nu_j) - \sum_i \nu_i (\epsilon_i + p\nu_i)$.

Kirchhoff's law

$$\left(\frac{\partial H}{\partial T} \right)_p = \sum_j \nu_j c_p^j - \sum_i \nu_i c_p^i \quad (6)$$

which also serves for the integration of (5) and finally *the dependence of K upon hydrostatic pressure*

$$\left(\frac{\partial \log K}{\partial p} \right)_T = \frac{1}{RT} \sum_i \nu_i V_i - \frac{1}{RT} \sum_j \nu_j V_j \quad (7)$$

A less well-known thermodynamic equation which might be considered to be the generalisation of (7) is the law

$$\left(\frac{\partial \log K}{\partial \chi} \right)_T = \frac{1}{RT} \sum_i \nu_i \beta_i - \frac{1}{RT} \sum_j \nu_j \beta_j = \frac{\beta_1 - \beta_2}{RT} \quad (8)$$

Here χ is some continuously variable parameter which can operate reversibly on the states 1 and 2, while β_1 and β_2 represent the derivatives with respect to χ of the free energies of states (1) and (2) respectively.

The proof equation of (8) is as follows :

The free energy of a system of molecules each species behaving ideally is

$$\phi = \sum_i n_i (\phi_i + RT \log c_i),$$

where n_i represents the number of gram molecules of species i ,

$$c_i = \frac{n_i}{\sum_i n_i + \sum_j n_j}$$

and ϕ_i the standard free energy of 1 gram molecule of i under standard condition of temperature and χ where χ includes hydrostatic pressure and all other possible parameters such as electric and magnetic fields, etc.

$$\phi_i = \epsilon_i + \chi \beta_i - TS_i.$$

a change in the electrode potential, and (3) a change in χ caused by a continuous change in the nature of the solvent. Of these cases the only one which is applicable free from hypothesis with respect to χ is realised when $\chi = \pi$. We have then equation (7) for equilibrium and

$$\frac{\partial \log k}{\partial \pi} = \frac{V_1 - V_r}{RT} \quad (7a)$$

for reaction velocities. Integrating (7) and (7a) on the assumption that $V_1 - V_2$ and $V_1 - V_r$ are independent of χ we obtain

$$\log K = \frac{(V_1 - V_2)}{RT} \pi + \text{const.} \quad (10)$$

$$\log k = \frac{(V_1 - V_r)}{RT} \pi + \text{const.} \quad (10a)$$

We have discussed the experimental evidence for (10a) in our previous paper; more recent measurements⁶ on the influence of pressure on the reaction between acetic anhydride and ethylalcohol give additional confirmation of the logarithmic dependence of k on π .

For higher pressures the square terms in π whose coefficients contain the compressibilities of the two states should be introduced into equation 10 and 10a.¹ In this paper we restrict ourselves to the linear terms in the integrated form of equations (8) and (8a). Thus we have

$$\log K = \frac{(\beta_1 - \beta_2)}{RT} \chi + \text{const.} \quad (11a)$$

$$\log k = \frac{(\beta_1 - \beta_r)}{RT} \chi + \text{const.} \quad (11b)$$

The second example of a continuous variation of χ is realised when χ is the electrode potential ϵ . (11a) then becomes the Helmholtz-Nernst equation in which $(\beta_1 - \beta_2)$ is $1/F$ and ϵ is the equilibrium potential.

On the other hand (11b) takes on the form of the Tafel's equation for the current i_1 passing in the direction $1 \rightarrow 2$ as a function of the electrode potential ϵ .

$$\log i_1 = \frac{\alpha(\epsilon/FRT)}{\alpha = \beta_1 - \beta_r} + \text{const.} \quad (12b)$$

Equations (10), (11) and (12) are examples of linear relationships between free energies in which the equilibrium constant on the left-hand side and the variable parameter multiplied by a constant on the right-hand side are different measures of the free energy. It is also clear that further relationships arise from a pair of equations (a) and (b) by eliminating χ . In doing this we will assume that the equations (a) and (b) refer to the same reaction. We have then

$$\log k_x = \alpha \log K_x + \text{const.} \quad (13)$$

where the subscript χ indicates that this variable has the same value for both sides of the equation. We also obtain

$$\alpha = \frac{\beta_1 - \beta_r}{\beta_1 - \beta_2} \quad (14)$$

and recognise that if the derivative of the free energy of the transition state β_r lies intermediate between the derivatives referring to the initial and final states, β_1 and β_2 , we have $\alpha < 1$.

⁶ *Proc. Roy. Soc., A*, 1936, 184, 684.

The influence of hydrostatic pressure on a reaction of the type $A + B \rightarrow AB$ is an example of a case in which $\alpha < 1$. Here the volume of the transition state V_τ might be expected to be intermediate between V_1 and V_2 . In the more detailed discussion of our previous communication we have also explained that V_τ is only slightly greater than V_2 .

The measurements of Perrin, Gibson and Williams⁶ show that the equilibrium of the reaction methylbenzylaniline + allylbromide \rightarrow phenylbenzylmethylallyl ammoniumbromide is changed by hydrostatic pressure to a greater extent than is the velocity constant, in consequence of which hydrostatic pressure is found to decelerate the reverse reaction, which means $\alpha < 1$.

Our expectation that the value of V_τ while lying between V_1 and V_2 is much nearer to the latter value ($\alpha \sim 1$) is borne out by the fact that the deceleration for the back reaction is only 1.5 fold for 3000 atm. increase in pressure, while for the forward reaction the acceleration is 5 fold for the same pressure change.

If for a reaction of this type the volumes V_1 and V_2 have been measured it can be predicted that $\frac{\partial \log k}{\partial \chi}$ will be less than, but almost equal to $(V_1 - V_2)/RT$.

Brönsted's treatment of the influence of electrolytes on reaction velocity which, as stated in our previous communication, represents one of the origins of the present theory can also be expressed in the form of equation (8a). Substituting the concentration c of an added electrolyte for χ

$$\frac{\partial \log K}{\partial c} = \frac{\beta_1 - \beta_2}{RT} \quad . \quad . \quad . \quad (16)$$

where $(\beta_1 - \beta_2)$ now means the change of the logarithms of the activity coefficients f of the states (1) and (2) with change in concentration.

$$\beta_1 = - \frac{\partial \log f_1}{\partial c}.$$

Again the equilibrium constant may refer to the equilibrium between the initial and final states of the reaction or between the initial and transition states; in which case, $\beta_\tau = - \frac{\partial \log f_\tau}{\partial c}$ where f_τ is equivalent to the activity coefficient of the "active complex" which Brönsted assumes. If β_1 , β_2 and β_τ are good constants we have for the integrated forms of (16)

$$\log K = \frac{(\beta_1 - \beta_2)}{RT} c + \text{const.}$$

$$\log k = \frac{(\beta_1 - \beta_\tau)}{RT} c + \text{const.}$$

From which, by the elimination of c , an equation of the form (2) can be obtained.

Similar equations might be suggested for the addition of non-electrolytes, or the progressive replacement of the solvent by another, perfectly miscible solvent.

4. Linear Relationships Accompanying Structural Changes and Series of Different Solvents.

Consider a series of chemical equilibria, *i.e.*, a set of reactions which are closely related chemically, *e.g.*, the hydrolytic equilibria of the different substituted phenyl acetates. We assume that the series of equilibrium constants $K_1, K_2 \dots K_j \dots$ arises according to equation (8a) by a steadily changing parameter χ which assumes successive values $\chi_1, \chi_2 \dots \chi_j \dots$.

At this stage we leave the nature of χ undefined, nor can we say what the physical meaning of the corresponding values of β may be. We only wish to show that these considerations lead to an explanation of the linear relationships mentioned in Section 1. For this purpose we extend the argument to a second series of reactions chemically related to the first.

Consider, for example, the equilibrium constants of the substituted phenyl acetates and of the same substituted series of benzoyl acetates. If the equilibrium constants for members of the first series are $K_1^A, K_2^A \dots K_j^A \dots$ and for the second series $K_1^B, K_2^B \dots K_j^B$ and moreover if we make the essential assumption that

$$\frac{\chi_1^A}{\chi_1^B} = \frac{\chi_2^A}{\chi_2^B} = \dots = \frac{\chi_j^A}{\chi_j^B} = \dots = q$$

where q is a constant, we obtain

$$\log K_i^A = \alpha \log K_i^B + \text{const.} \quad (i = 1, 2, \dots, j \dots) \quad (17)$$

where
$$\alpha = q \frac{(\beta_1 - \beta_2)^A}{(\beta_1 - \beta_2)^B}.$$

This argument can be extended to two series of the velocity constants of closely related series by using equation (11b); we thus obtain

$$\log k_i^A = \alpha \log k_i^B + \text{const.} \quad (i = 1, 2, \dots, j \dots) \quad (18)$$

where
$$\alpha = q \frac{(\beta_1 - \beta_7)^A}{(\beta_1 - \beta_7)^B}$$

and a third type of linear relationship is derived from the combination of a series of equilibrium constants with a series of reaction velocity constants.

$$\log k_i^A = \alpha \log K_i^B + \text{const.} \quad (i = 1, 2, \dots, j \dots) \quad (19)$$

where
$$\alpha = q \frac{(\beta_1 - \beta_7)^A}{(\beta_1 - \beta_2)^B}.$$

We cannot as yet test the expressions for α but we enumerate the main cases conforming to equations (17) to (19).

An example of the type expressed in equation (17) is given by Burkhardt, Ford and Singleton⁷ where K_i^A represents the dissociation constants of a series of substituted phenyl acetic acids and the K_i^B the dissociation constants of the same series of benzoic acids.

Linear relationships of the type (18) can also be inferred from that given by Burkhardt, Ford and Singleton, since the logarithms of the velocity constants of the following reactions all give linear relationships with respect to the logarithms of the dissociation constants of the corresponding benzoic acids: acid catalysed hydrolysis of the substituted

⁷ *J. Chem. Soc.*, 1936, p. 17.

potassium phenylsulphates, alkaline hydrolysis of the corresponding benzamides, alkaline hydrolysis of the corresponding ethylbenzoates, hydrolysis of the corresponding benzylchlorides by aqueous alcohol, alkaline hydrolysis of the corresponding ethylcinnamates, bromination of the corresponding acetophenones and the reaction



for corresponding groups X.

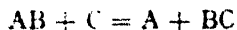
Equation (19) expresses Brönsted's law to which we have referred in the first section. As another example, Dimroth⁸ related the velocity constants of oxidation of a series of hydroquinones to the equilibrium constants of the corresponding quinone-hydroquinone reaction. Further cases have been found by Hammett and the results of Burkhardt, Ford and Singleton⁷ to which we have just referred also conform to equation (19).

If, in equation (19), k and K refer to the same reaction we obtain a special case similar to that described by equation (13) for the variations of a continuous parameter. We have shown by the example of hydrostatic pressure that the relationship between $\frac{\partial \log k}{\partial \chi}$ and $\frac{\partial \log K}{\partial \chi}$ referring to the same reaction is found to be considerably simplified, when the mechanism of the reaction is such that β_r has a value intermediate between β_1 and β_2 and hence $\alpha < 1$.

The condition $\alpha < 1$ has been found in various other important cases. It has been much discussed as a feature of Tafel's equation governing the rate of electrolytic evolution of hydrogen and other electrode processes, and has been found in acid-base catalysis (Brönsted) as well as in other proton transfers such as hydroquinone reduction (Dimroth).

Following on the lines of theory of ionogenic processes developed by Ogg and Polanyi,⁹ an outline of the mechanism of such proton transfers was given by Horiuti and Polanyi¹⁰ which led to an explanation of $\alpha < 1$ on the assumption that reaction rate is completely determined by the energies of the transition state. The identification of energy and free energy implied in this treatment would be correct at the absolute zero of temperature only, and otherwise requires qualifications which are discussed in Section 10 below.

At the moment we only wish to restate in thermodynamical terms the main conception of the theory. If a parameter χ operating on a reaction



the influence of χ is restricted to *one* of the two bonds involved, the condition that β_r is intermediate between β_1 and β_2 will be fulfilled, and we have $\alpha < 1$ provided that χ is approximately constant over the range of elongations occurring in the affected bond.¹¹ Variation of the

⁸ *Z. angew. Chemie*, 1933, 46, 571.

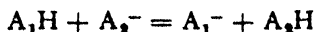
⁹ *Proc. Manchester Lit. Phil. Soc.*, 1933-34, 78, 41; *Trans. Faraday Soc.*, 1935, 31, 604; *ibid.*, 1935, 31, 1375.

¹⁰ *Acta Physico Chemica, U.S.S.R.*, 1935, 2, 505.

¹¹ It is essential that the reaction should be of the "electron switch" type, i.e. involving a change in electronic structure such as the formation of ions or a change in the valence of one or more of the reacting partners. In the next paper of this series we will show that reactions in which changes of this type occur, affecting a number of electrons, generally lead to a small perturbation energy in the transition state. (See *Trans. Faraday Soc.*, 1935, 31, 1375.)

chemical nature of A or of C alone will generally fulfil these requirements attached to χ , while chemical modification of B will fail to do so.

A discontinuous series of χ 's can be represented by a *series of solvents*. Such series may conform to the linear relationships set out above. Thus, equation (17) has been found to hold by Wynne-Jones¹² for the equilibrium constants of the reactions



which he describes as the relative dissociation constants of the acids A_1H and A_2H ; the linear dependency of such equilibrium constants on the reciprocal of the dielectric constants of the solvent implies a linear relationship between the equilibrium constants. We shall discuss the relation to the dielectric constant at a later stage.

Dimroth¹³ provides evidence as to the changes in velocity and equilibrium constants for a reaction occurring in a series of solvents. Although these data do not comply quantitatively with equation (19) they definitely show a close parallelism of $\log K$ and $\log k$. Here again the variations of $\log k$ are smaller than the variations of $\log K$, thus corresponding to $\alpha < 1$. Thus, it is apparent that the changes of solubility of the transition state from solvent to solvent are intermediate between those of the initial and final states.

Soper¹⁴ has observed that reactions in which heteropolar substances are formed are promoted by solvents of a heteropolar nature. Soper's rule becomes understandable if we again assume that the changes in solubility of the transition are intermediate between those of the initial and final states, so that the solubility of the transition state increases with that of the final state.*

5. Linear Relationships Including Heat Changes.

In equations (9) and (9a) we gave the expression for the influence of changes of the parameter χ on the heat of reaction, and the activation energy.

Equations (9) and (9a) give on integration, assuming that $\gamma_2 - \gamma_1$ and $\gamma_\tau - \gamma_1$ are constants with respect to χ

$$\begin{aligned} \text{and} \quad H &= (\gamma_2 - \gamma_1)\chi + \text{const.} \\ Q &= (\gamma_\tau - \gamma_1)\chi + \text{const.} \end{aligned} \quad (20)$$

and by eliminating χ we have

$$\begin{aligned} Q &= \alpha H + \text{const.} \\ \alpha &= (\gamma_1 - \gamma_\tau)/(\gamma_1 - \gamma_2). \end{aligned}$$

If χ is the hydrostatic pressure π then

$$\begin{aligned} \gamma_1 - \gamma_2 &= -T \left(\frac{\partial(V_1 - V_2)}{\partial T} \right)_\pi + (V_1 - V_2) \\ \gamma_1 - \gamma_\tau &= -T \left(\frac{\partial(V_1 - V_\tau)}{\partial T} \right)_\pi + (V_1 - V_\tau). \end{aligned}$$

¹² *Proc. Roy. Soc., A*, 1933, 140, 440.

¹³ *Lieb. Ann.*, 1910, 377, 128.

¹⁴ Soper and collaborators; *J. Chem. Soc.*, 1929, 1873; 1931, 2297; *Proc. Roy. Soc., A*, 1933, 140, 58, 71; 1934, 144, 643.

* The relationships between solubilities and chemical free energies are detailed in Section 6.

For the change in heat of reaction with pressure we require not only the volume of the initial and final states but also their expansion coefficients; while for the change in activation energy it is necessary to know the volume and expansion coefficient of the transition state. One might expect $\left(\frac{\partial V_{\tau}}{\partial T}\right)_{\pi}$ to lie between the values for the initial and final states,

in analogy to the position of V_{τ} between V_1 and V_2 discussed in Section 3.

If we compare the activation energy and the reaction velocity constant at constant values of the parameter χ

$$-\frac{Q_{\tau}}{RT} = \alpha \log k_{\tau} + \text{const.},$$

where

$$\alpha = \frac{\gamma_1 - \gamma_{\tau}}{\beta_1 - \beta_{\tau}}.$$

For $\chi = \pi$

$$\alpha = 1 - \frac{T}{V_1 - V_{\tau}} \left(\frac{\partial(V_1 - V_{\tau})}{\partial T} \right)_{\pi}.$$

If the effect of a parameter, *e.g.*, of the hydrostatic pressure on reaction rate were restricted to changes of the activation energy, we would have $\alpha = 1$. Our expression for α shows that there is no reason to assume that this should be generally true. We shall see in Section 9 that $\alpha = 1$ at absolute zero only.

By eliminating χ from equations (11a), (11b), (20) and (21) we obtain linear relationships between the heat of reaction, the activation energy, the logarithm of the equilibrium constant and the logarithm of the velocity constant of the same reaction for constant values of χ ; a conclusion which can most easily be verified for $\chi = \pi$, the hydrostatic pressure.

To consider discontinuous changes in the parameter we assume that $H_1^A, H_2^A, \dots, H_j^A, \dots$ are a series of heats of reaction for a reaction of the type A arising from the influence of a steadily changing parameter, when χ has the values $\chi_1, \chi_2, \dots, \chi_j, \dots$. Now $H_1^B, H_2^B, \dots, H_j^B$ are the heats of reaction for an analogous reaction of type B when χ has the same values $\chi_1, \chi_2, \dots, \chi_j, \dots$. Again, making the assumption that the influence of χ on the two types A and B is of the form $\frac{H_1^A}{H_1^B} = \frac{H_2^A}{H_2^B} = \dots = \frac{H_j^A}{H_j^B} = \text{const.} = q$, we obtain from equations (9) and (20)

$$\left. \begin{aligned} H_i^A &= \alpha H_i^B + \text{const.} \quad i = 1, 2, \dots, j, \dots \\ \alpha &= q \frac{(\gamma_1 - \gamma_{\tau})^A}{(\gamma_1 - \gamma_{\tau})^B} \end{aligned} \right\} \quad (21)$$

The extensions of this expression are:—

$$\left. \begin{aligned} Q_i^A &= \alpha Q_i^B + \text{const.} \quad i = 1, 2, \dots, j, \dots \\ \alpha &= q \frac{(\gamma_1 - \gamma_{\tau})^A}{(\gamma_1 - \gamma_{\tau})^B} \end{aligned} \right\} \quad (22)$$

relating the activation energies of the members of the two series A and B.

$$\left. \begin{aligned} Q_i^A &= \alpha H_i^B + \text{const.} \quad i = 1, 2, \dots, j, \dots \\ \alpha &= q \frac{(\gamma_1 - \gamma_{\tau})^A}{(\gamma_1 - \gamma_{\tau})^B} \end{aligned} \right\} \quad (23)$$

relating the activation energy and the heat of reaction. A special case of this is where A and B refer to the same reaction, when as before we may assume $\frac{\chi_1^A}{\chi_1^B} = \frac{\chi_2^A}{\chi_2^B} = \dots = \frac{\chi_r^A}{\chi_r^B} = \dots = 1$ then $\alpha = \frac{\gamma_1 - \gamma_r}{\gamma_1 - \gamma_2}$; in the special cases where γ_r lies intermediate between γ_1 and γ_2 , α will be < 1 .

By combining equations (21), (22) and (23) for special values of the parameter χ with those arising from (8) and (8a) for the same values of the parameter $\chi = \chi_1, \chi_2 \dots \chi_r \dots$, we have the following set of linear relationships between chemical free energies and heat changes in chemical reactions:

$$\left. \begin{aligned} -\frac{H_i^A}{RT} &= \alpha \log K_i^B + \text{const.} \\ \alpha &= q \frac{(\gamma_1 - \gamma_2)^A}{(\beta_1 - \beta_2)^B} \end{aligned} \right\} \dots \dots \dots (24)$$

relating the heat of reaction and the equilibrium constant;

$$\left. \begin{aligned} -\frac{Q_i^A}{RT} &= \alpha \log k_i^B + \text{const.} \\ \alpha &= q \frac{(\gamma_1 - \gamma_r)^A}{(\beta_1 - \beta_r)^B} \end{aligned} \right\} \dots \dots \dots (25)$$

relating the activation energy and the velocity constant;

$$\left. \begin{aligned} -\frac{Q_i^A}{RT} &= \alpha \log K_i^B + \text{const.} \\ \alpha &= q \frac{(\gamma_1 - \gamma_r)^A}{(\beta_1 - \beta_r)^B} \end{aligned} \right\} \dots \dots \dots (26)$$

relating the activation energies and the equilibrium constant;

$$\left. \begin{aligned} -\frac{H_i^A}{RT} &= \alpha \log k_i^B + \text{const.} \\ \alpha &= q \frac{(\gamma_1 - \gamma_2)^A}{(\beta_1 - \beta_2)^B} \end{aligned} \right\} \dots \dots \dots (27)$$

relating the heat of reaction and the velocity constant.

From the work of Wynne-Jones¹² we have so far only adduced the linear relationship between the logarithms of the equilibrium constants for the reaction $A_1H + A_2^- = A_2H + A_1^-$. He also found that $\log K = \alpha 1/D + \text{const.}$, where D is the dielectric constant of the medium. This result conforms with equation (24), since there is no other way of interpreting the observed influence of the dielectric constant than to set $1/D \propto H$, i.e. the difference in solution energies of a pair of anions A_1 and A_2 must be proportional to $1/D$. This interpretation is implied in the original discussions by Wynne-Jones and in the modified treatment given by Wootten and Hammett.¹³ The results of Wynne-Jones naturally also conform to equation (21) which follows from (17) and (24). Further evidence with respect to equation (24) will be given in the next section which deals with the equilibria of solvents and solutes.

An indication of the validity of equation (27) is given by the evidence

¹³ J. Amer. Chem. Soc., 1935, 57, 2289

which has been put forward in support of the theorem of Ogg and Polanyi requiring a parallelism between reaction heat and reaction velocity. Quantitative data are, however, lacking for its exact verification; this should also include a test of equation (23), which is the original form in which the theorem was obtained from considerations of the reaction mechanism (compare Section II).

Equation (25) might at first sight appear trivial since it necessarily holds in so far as the collision number is invariant. In many cases which we wish to consider the collision number is far from constant and yet, as we shall see, equation (25) holds. To bring this out it might be preferable to substitute for (25) an equivalent expression which refers explicitly to the change in collision number. We do this first with reference to the general case of equilibrium constants and heats of reaction and then make the special application to velocity constants and activation energies.

By combining equations (8a) and (9a) we obtain

$$\frac{\partial(RT \log K + H)}{\partial \chi} = (\beta_1 - \beta_2) + (\gamma_2 - \gamma_1). \quad (28)$$

If $\beta_1, \beta_2, \gamma_1$ and γ_2 are constant with respect to χ

$$RT \log K + H = (\delta_1 - \delta_2)\chi + \text{const.} \quad (28)$$

setting $(\beta_1 - \gamma_1) = \delta_1$ and $(\beta_2 - \gamma_2) = \delta_2$.

By eliminating χ from (28) and (20) we obtain

$$RT \log K + H = \alpha H + \text{const.} \quad (29)$$

where $\alpha = \frac{\delta_1 - \delta_2}{\gamma_2 - \gamma_1}$.

For discontinuous values of the parameter we have

$$\frac{S_i^A}{R} = \log K_i^A + \frac{H_i^A}{RT} = \alpha \frac{H_i^B}{RT} + \text{const.} \quad (i = 1, 2, \dots, j, \dots), \quad (30)$$

where A and B represent two types of chemically analogous reactions.

We are only interested at the moment in the form of (30) relating to equation (25), i.e. to reaction velocities and activation energies:

$$\left. \begin{aligned} \frac{s_i^A}{R} &= \log k_i^A + \frac{Q_i^A}{RT} = \alpha \frac{Q_i^B}{RT} + \text{const.} \quad (i = 1, 2, \dots, j, \dots) \\ \alpha &= q \frac{(\delta_1 - \delta_2)^A}{(\gamma_2 - \gamma_1)^B} \end{aligned} \right\} \quad (31)$$

where both in equations (30) and (31) we have assumed

$$\frac{\chi_1^A}{\chi_1^B} = \frac{\chi_2^A}{\chi_2^B} = \dots = \frac{\chi_j^A}{\chi_j^B} = \dots = q,$$

and in (31) the symbol s is used to represent the entropy change between the initial and transition states.

Equation (31) is to some extent supported by the results of Olivier¹⁰ for the hydrolysis of the substituted benzylchlorides by aqueous alcohol

¹⁰ *Rec. Trav. Chim.*, 1923, 42, 775; 1927, 46, 1229.

which we have plotted in Fig. 1 and also the work of Burkhardt, Ford

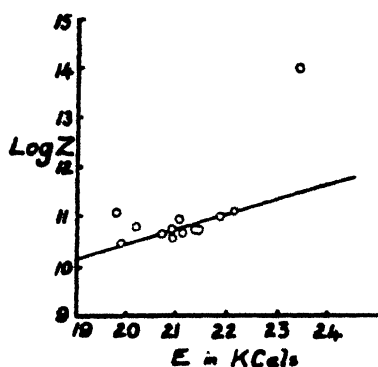


FIG. 1.

and Singleton⁷ on the acid catalysed hydrolysis of the substituted phenyl sulphates. It is significant that both these reactions also follow the linear relationship (19) which has been deduced from the same assumptions. The joint verification of the two linear relationships tends to support the assumptions on which they are both based.

Equation (26) is already verified by the fact that both equation (19) and (25) are obeyed by the same series of substances, since from (19) and (25) we obtain (26) by expressing $\log k$ in terms of $\log K$.

6. Relationship between Entropies and Heats of Solution.

We have reserved for a special discussion the relationship between the equilibria of solutes in different solvents. From the experimental data given in literature we have found that in this field there is linear relationship between entropy and heat of solution.

If $H_1^A, H_2^A, \dots, H_j^A, \dots$ are the heats of solution of substance A in a series of solvents $i = 1, 2, \dots, j, \dots$ and $K_1^A, K_2^A, \dots, K_j^A, \dots$ are the corresponding equilibrium constants for the solution process we obtain in a manner similar to that in Section 5

$$-\frac{H_i^A}{RT} = \alpha \log K_i^A + \text{const.} \quad (i = 1, 2, \dots, j, \dots),$$

$$\alpha = \frac{(\gamma_1 - \gamma_2)^A}{(\beta_1 - \beta_2)^A}.$$

Similarly, if $H_A^i, H_B^i, \dots, H_P^i, \dots$ are the heats of solution of substances A, B, ..., P, ... in the solvent i and $K_A^i, K_B^i, \dots, K_P^i, \dots$ the corresponding equilibrium constants then

$$-\frac{H_P^i}{RT} = \alpha \log K_P^i + \text{const.} \quad (P = A, B, \dots),$$

$$\alpha = \frac{(\gamma_1 - \gamma_2)^i}{(\beta_1 - \beta_2)^i}.$$

We can write these equations in the form of equation (30) relating entropy and heat changes.

$$\left. \begin{aligned} \frac{S_i^A}{R} &= \alpha \frac{H_i^A}{RT_i} + \text{const.} \\ \alpha &= \frac{(\delta_1 - \delta_2)^A}{(\gamma_2 - \gamma_1)^A} \end{aligned} \right\} \quad (32)$$

$i = 1, 2, \dots, j, \dots$ while A is constant and

$$\left. \begin{aligned} \frac{S_P^i}{R} &= \alpha \frac{H_P^i}{RT} + \text{const.} \\ \alpha &= \frac{(\delta_1 - \delta_2)^i}{(\gamma_2 - \gamma_1)^i} \end{aligned} \right\} \quad (33)$$

P = A, B, ... while i is constant.

In Table I. we have listed the heats and entropies of solution for a number of solutes for each of which the solubilities and heats of solu-

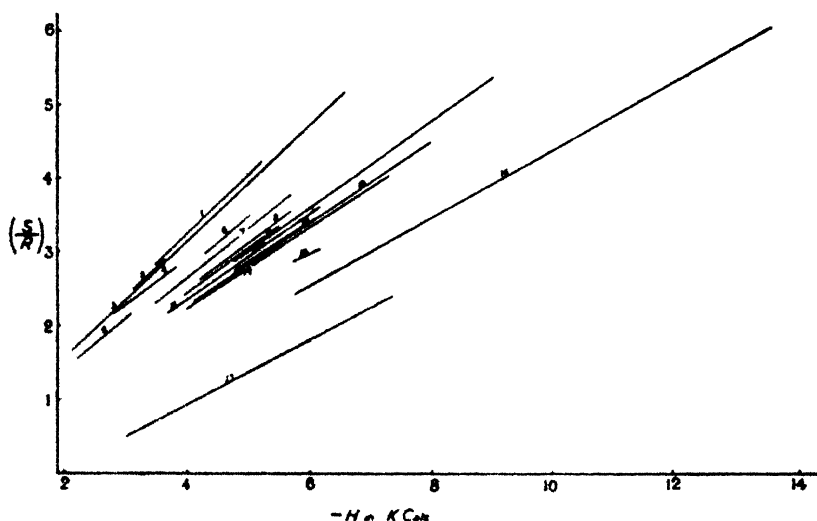


FIG. 2.—Key to Solutes: 1. Benzoyl chloride; 2. Nitrobenzene; 3. Benzene; 4. Ethylene; 5. Phenol; 6. *o*-Nitrophenol; 7. *o*-Chloroacetic acid; 8. Naphthalene; 9. *m*-Dinitrobenzene; 10. Acenaphthene; 11. Phenanthrene; 12. *o*-Dinitrobenzene; 13. Fluorene; 14. Benzoic acid; 15. *p*-Dinitrobenzene; 16 and 17. Carbazole

tion have been determined in various solvents. The data comprise all the measurements known to us. The heat and entropy changes are measured with the solute in its normal solid state as zero. In the last column the ratio of entropy and heat is given. With the exceptions of anthracene and carbazole the linear relationship (32) as expressed by a constant value of $\rho = \frac{\alpha}{RT}$ and c in the equation

$$\frac{S}{R} = \rho H + c$$

TABLE I.— $(S/R = \rho H + C$ FOR VARIOUS SOLUTES.)

Solvent.	H cal./mol.	S/R .	S/R calc.
* Benzoic Acid. ($H^\circ = 15,270$, $S^\circ = 9.03$, $\rho = 5.43 \times 10^{-4}$, $C = 0.057$.)			
Metahydroxy benzaldehyde	7260	4.030	3.998
Carbon tetrachloride	7140	3.955	3.836
Naphthalene	5740	3.182	3.177
Nitrobenzene	5510	3.055	3.055
Benzil	5170	2.865	2.866
Piperonal	4660	2.589	2.589
Acetic acid	4420	2.450	2.457
Acetophenone	4360	2.420	2.424
<i>o</i> -Chloroacetic acid	4240	2.357	2.357
<i>o</i> - <i>m</i> - and <i>p</i> -Chlorobenzoic acid	4130	2.290	2.319
Cinnamic acid	3980	2.209	2.217
Naphthalene. ($H^\circ = 15,890$, $S^\circ = 10.75$, $\rho = 6.16 \times 10^{-4}$, $C = 0.016$.)			
Acetone	5660	3.513	3.505
Ethyl ether	5370	3.326	3.326
Ethyl acetate	5310	3.282	3.295
Carbon tetrachloride	5100	3.159	3.159
Ethylene dibromide	4420	2.739	2.739
Pyridine	4380	2.717	2.717
Dichloroethane	4360	2.702	2.703
Chloroform	4200	2.598	2.605

* Solutes are set in heavy type at the top of each table of solvents.

TABLE I.—*Continued.*

Solvent.	H cal./mol.	S/R .	S/R calc.
Phenanthrene. ($H^\circ = 18,000$, $S^\circ = 12.09$, $\rho = 5.84 \times 10^{-4}$, $c = 0.016$.)			
Carbon disulphide	6090	3.767	3.562
Ethyl acetate	5930	3.534	3.476
Carbon tetrachloride	5620	3.309	3.000
Acetone	5280	3.096	3.096
Ethyl ether	5170	2.968	3.036
Pyridine	4260	2.502	2.502
Chloroform	3880	2.280	2.281
Tetrachloroethane	3660	2.152	2.155

***o*-Dinitro benzene.** ($\rho = 5.34 \times 10^{-4}$, $c = 0.102$.)

Benzene	8000	4.492	4.442
Phenanthrene	6230	3.515	3.482
Acenaphthene	5740	3.163	3.220
Naphthalene	5570	3.135	3.128
2-4-6 Trinitrotoluene	5470	3.068	3.075
1-3-5- Trinitrobenzene	5420	3.041	3.044
2-4 Dinitrotoluene	5390	3.030	3.031
<i>m</i> -Dinitrobenzene	5370	3.016	3.021
Fluorene	5320	2.987	2.993
β -Naphthylamine }	4970	2.790	2.803
α -Naphthylamine }			

Benzene. ($H^\circ = 10,560$, $S^\circ = 10.33$,
 $\rho = 7.84 \times 10^{-4}$, $c = 0.000$.)

Phenol	6570	5.160	5.150
Nitrobenzene	3100	2.432	2.431
Diphenylamine	2930	2.314	2.293
Benzoylchloride	2790	2.189	2.188
2-4, 2-6 and 3-4 Dinitrotoluene	2750	2.155	2.155
<i>m</i> -Dinitrobenzene	2750	2.155	2.155
<i>o</i> - <i>m</i> - and <i>p</i> -Bromonitrobenzene	2750	2.152	2.155
Nitrobenzylchloride	2720	2.124	2.127
Pyridine	2710	2.124	2.124
<i>o</i> -, <i>m</i> - and <i>p</i> -Chloronitrobenzene	2680	2.199	2.099
Bromoform	2590	2.028	2.030
Dibromoethane	2500	1.959	1.959
Paraldehyde	2360	1.849	1.849
Dichloroethane	2380	1.798	1.860
Camphene	2120	1.662	1.662

Acenaphthene. ($\rho = 5.87 \times 10^{-4}$, $c = 0.040$.)

Acetone	9060	5.390	5.36
Aniline	7910	4.700	4.69
Carbon tetrachloride	6640	3.945	3.94
Pyridine	6570	3.881	3.90
<i>o</i> -Dinitrobenzene	5800	3.468	3.45
Carbon disulphide	5660	3.362	3.36
Nitrobenzene	5470	3.246	3.248
Toluene	5440	3.233	3.232
<i>p</i> -Dinitrobenzene	5340	3.188	3.177
Indene	5250	3.121	3.121
Chlorobenzene	5220	3.098	3.107
Fluorene	4990	2.961	2.967
Chloroform	4850	2.880	2.880
Bromoacenaphthene	4770	2.859	2.841
Chloroacenaphthene	4750	2.843	2.831
Iodoacenaphthene	3400	2.214	2.039

is obeyed extremely well. The data for carbazole appear to lie on two straight lines of equal slope which cover different regions of the energy and entropy scales. Fig. 2 gives a general survey of the results listed in the tables.

Table II. comprises the heat and entropy changes of a series of solutes in the same solvent. In this case all the changes are measured taking the solutes under standard conditions in the vapour state as the zero energy and entropy. The scope of validity of equation (33) which applies to this case has been found to be limited to solutes which belong to the same chemical group. Table II. does not contain all the available material, but only a selection of data referring to such groups.

The narrower range of validity of (33) indicates that variations of the solute cannot generally be regarded as changes in a parameter with respect to which the deriva-

TABLE I.—Continued.

Solvent.	H cals./mol.	S/R .	S/R calc.
Carbazole. ($\rho = 4.57 \times 10^{-4}$, $c = -0.221$.)			
Pyrogallol	1410	6.047	6.219
Resorcinol	1220	5.227	5.339
Catechol	1030	4.427	4.479
<i>p</i> -Nitrophenol	8240	3.541	3.547
α -Naphthol	7110	3.059	3.036
<i>m</i> -Nitrophenol	7900	3.395	3.397
β -Naphthol	7960	3.430	3.420
Chrysine	6800	2.873	2.889
<i>o</i> -Nitrophenol	6540	2.807	2.768
Nitrobenzene	5740	2.397	2.402
($\rho = 4.57 \times 10^{-4}$, $c = -1.000$.)			
Carbon tetrachloride	7320	2.406	2.40
Carbon disulphide	6580	1.972	2.10
Acetic acid	6090	1.780	1.78
Acetone	2960	0.595	0.35
Nitrobenzene. ($H^\circ = 14.490$, $S^\circ = 10.96$, $\rho = 7.79 \times 10^{-4}$, $c = 0.022$.)			
Phenol	3660	2.871	2.872
Benzoyl chloride	3330	2.608	2.619
Benzene	3140	2.481	2.469
<i>o</i> -, <i>m</i> - and <i>p</i> -Nitraniline	3140	2.477	2.469
Naphthalene	3140	2.477	2.469
<i>o</i>-Nitrophenol. ($\rho = 6.96 \times 10^{-4}$, $c = -0.042$.)			
<i>p</i> -Nitrophenol	5080	3.470	3.498
Naphthalene	5000	3.442	3.440
<i>m</i> -Nitrophenol	4900	3.380	3.369
β -Naphthylamine	4810	3.310	3.307
α -Naphthylamine	4460	3.072	3.060
<i>p</i> -Toluidine	4300	2.953	2.957
Picric acid	4270	2.934	2.934
<i>p</i>-Dinitrobenzene. ($\rho = 4.13 \times 10^{-4}$, $c = 0.472$.)			
Fluorene	6170	3.033	3.023
Anthracene	5900	2.905	2.912
Acenaphthene	5710	2.824	2.732
<i>m</i>-Dinitrobenzene. ($\rho = 5.94 \times 10^{-4}$, $c = 0.030$.)			
Acetanilide	5500	3.307	3.292
Benzene	4910	2.921	2.949
1-3-5 Trinitrobenzene	4300	2.588	2.588
2-4 Dimittrotoluene	4190	2.524	2.518
<i>o</i> -Dinitrobenzene	4050	2.438	2.433
Picric acid	3950	2.372	2.374
Fluorene	4220	2.547	2.537
α-chloroacetic. ($\rho = 6.55 \times 10^{-4}$, $c = -0.017$.)			
<i>o</i> -, <i>m</i> - and <i>p</i> -cresol	5760	3.748	3.757
Salol	5470	3.562	3.565
<i>o</i> -Toluic acid	5060	3.211	3.299
Phenol	4980	3.257	3.245
Benzoic acid	4840	3.142	3.148
<i>m</i> - and <i>p</i> -Toluic acid	4720	3.177	3.077
Cinnamic acid	4390	2.866	2.862
Crotonic acid	3980	2.598	2.591
Phenyl acetic acid	3860	2.523	2.512
Acetic acid	3500	2.284	2.276

tives of free energy and energy are constant. In other words, while in accordance with equation (32), solubility is found to be a unique function of solution heat for a given solute in varying solvents, this is not generally so for different solutes in the same solvent. Thus it appears that the phase volume of different solutes is different in the same solvent, even if the heat of solution is the same, whereas equal heats are accompanied by equal phase volumes if a substance is dissolved in different solvents.

The following conclusion seems interesting: considering the distribution of a solute between its vapour phase and its solutions in various solvents, i.e. the solubility of the vapour in these solvents, we realise that the "thermo-neutral solubility" of the vapour which would arise if the intermolecular forces between solute and solvent

TABLE I.—Continued.

Solvent.	<i>H</i> cal./mol.	<i>S/R</i> .	<i>S/R</i> calc.
Benzoyl chloride. ($\rho = 8.06 \times 10^{-4}$, $c = -0.023$.)			
Nitrobenzene	5260	4.218	4.222
Diphenyl	3890	3.118	3.117
Benzene	3740	3.008	2.995
<i>p</i> -Xylene	3740	3.008	2.995
Diphenylmethane	3670	2.940	2.937
Mesitylene	3600	2.890	2.882
Chlorobenzene	3480	2.790	2.786

Ethylene dibromide. ($\rho = 6.05 \times 10^{-4}$, $c = 0.466$.)

<i>p</i> -Bromotoluene	3790	2.767	2.753
Paraldehyde	2980	2.304	2.268
<i>p</i> -Xylene	2800	2.163	2.161
Benzene	2760	2.128	2.137
Diphenylamine	2760	2.128	2.137
Naphthalene	2730	2.113	2.117

Phenol. ($H^{\circ} = 14,590$, $S^{\circ} = 11.32$, $\rho = 6.92 \times 10^{-4}$, $c = 0.008$.)

Benzene	3070	2.142	2.135
Acetic acid	2980	2.078	2.072
Nitrobenzene	2580	1.795	1.790
α -Chloroacetic acid	2470	1.708	1.718
<i>m</i> -Hydroxybenzaldehyde	2190	1.525	1.520

Fluorene. ($\rho = 5.63 \times 10^{-4}$, $c = 0.006$.)

Acetone	7290	4.078	4.096
Carbon tetrachloride	6100	3.448	3.437
Pyridine	5480	3.097	3.087
Benzene	5380	3.031	3.031
Toluene	5380	3.031	3.031
Xylene	5380	3.031	3.031
Aniline	5320	3.808	3.002
Nitrobenzene	5100	2.880	2.874
Chlorobenzene	5050	2.851	2.846
Indene	5010	2.826	2.826
<i>o</i> -Dinitrobenzene	4800	2.723	2.706
Acenaphthene	4440	2.507	2.506
Naphthalene	4320	2.438	2.458
2,4-Dinitrophenol	4190	2.366	2.366
<i>m</i> -Dinitrophenol	4160	2.236	2.346

could be annulled, would be equal for any solute in all solvents, but equal only for a group of chemically related solutes when compared in the same solvent.

7. Collision Factors in Solution.

In our previous paper we have pointed out that a generalisation of Wigner's method of calculating "collision numbers" yields

$$k = \frac{1}{2} K v,$$

where the equilibrium constant K between the initial state and the transition state can be calculated if the atomic model of both states is completely known, for solutions the atomic model should include the structure of the solvent sheath in both states. Since our know-

ledge of the structure of solutions is as yet insufficient to enable us to calculate the entropy changes in the solvent sheath we have adopted the method of calculating first the collision number in the gas phase and then relating it through the entropies of solution of the reactants and

TABLE II.

Nitrobenzene. ($\rho' = 4.05 \times 10^{-4}$, $c = 2.19$.)

Solute.	<i>H</i> cal./mol.	<i>S/R</i> .	<i>S/R</i> calc.
Benzoic acid	9750	5.98	6.13
<i>o</i> -Nitraniline	12650	7.22	7.30
<i>m</i> -Nitraniline	15100	8.44	8.29
<i>p</i> -Nitraniline	17300	9.18	9.36

the transition state to the collision number in solution. This procedure has shown that the "slowness" of many reactions which has been noted by Moelwyn-Hughes and Hinshelwood¹⁷ can be accounted for in the cases of association reactions by the smallness of the collision factor of these reactions calculated for the gas phase. This conclusion has received support by the observations of Wassermann¹⁸ that a number of association reactions have the same abnormally low collision number in the gas phase as they have in solution.

The large variations which are known to occur in the collision number when reactions are measured in different solvents and also under the influence of hydrostatic pressure, show that the collision number in solution and in the gas phase cannot in general be the same.

In this Section we wish to deal with the influence of solution on the collision number which we assume to be known for the gas phase, by extending the argument given on this subject in our previous paper.

If K' represents the equilibrium constant in solution and K the equilibrium constant in the gas phase we have for the reaction $A + B \rightarrow C$

$$K' = K \frac{x_C}{x_A x_B}$$

where x_A , x_B and x_C are the solubilities of the vapours A, B and C. Or, for equilibrium constants of the transition state

$$K' = K \frac{x_T}{x_A x_B},$$

where x_T is the solubility of the transition state, and with the approximation that v is not influenced by the presence of the solvent

$$k' = k \frac{x_T}{x_A x_B}$$

in the terms used in this paper we write

$$\log k' = \log k - \frac{H_T}{RT} + \frac{S_T}{R} + \frac{H_A}{RT} - \frac{S_A}{R} + \frac{H_B}{RT} - \frac{S_B}{R}$$

$$\log Z' = \log Z + \frac{S_T}{R} - \frac{S_A}{R} - \frac{S_B}{R}$$

where $Q' = Q + H_T - H_A - H_B$

where Z' and Z are the collision numbers in solution and in the gas phase respectively.

For a numerical comparison of Z' and Z we introduce the unit of mol./litre both for the gas phase and solution, we have then

$$\log \frac{Z'}{Z} = \frac{1}{R}(S_T - S_A - S_B) - \log \frac{\Delta}{M} 10^3, \quad (34a)$$

where M and Δ are the molecular weight and the density of the solvent.

If S° and S^\bullet are the entropy of solution and the entropy of vaporisation of the solid solute (34a) becomes

$$\log \frac{Z'}{Z} = \frac{1}{R}((S_T^\bullet - S_T^\circ) - (S_A^\bullet - S_A^\circ) - (S_B^\bullet - S_B^\circ)) - \log \left(\frac{1.7\Delta}{M} 10^3 \right) \quad (34b)$$

¹⁷ *J. Chem. Soc.*, 1932, p. 230.

¹⁸ Wassermann, *Nature*, 1936, **137**, 497.

The tables given in the previous Section provide ample material to discuss the possible variations of Z'/Z if we assume that the substances A, B and the transition complex behave in a manner similar to the substances listed there. Taking benzene as a substance representative of a wide range of heats and entropies of solution we might assume for the moment that A, B and the complex all behave like benzene. From the values given in the table and the entropy of evaporation of benzene we calculate for two solvents taken from the extremes of the complete range, *vis.*, bromoform and phenol the values $S/R = 8.38$ and 5.18 respectively. Introducing

$$\frac{S_A}{R} = \frac{S_B}{R} = \frac{S_T}{R} = 8.38,$$

we obtain $Z'/Z = 1.2 \times 10^3$, while for phenol with

$$\frac{S_A}{R} = \frac{S_B}{R} = \frac{S_T}{R} = 5.18,$$

we obtain $Z'/Z = 0.89$.

Thus we see that the collision numbers in the gas phase and in solution will in general be different and also that we might expect the occurrence of collision numbers in solution greater than those in the gas phase.¹⁹

If one of the reactants is the solvent and we assume that the reactant A and the transition state behave in the same way equation (34b) becomes

$$\log \frac{Z'}{Z} = - \frac{(S_B^\circ - S_B^s)}{R} - \log \frac{1.7\Delta}{M} 10^7.$$

When B is the solvent $(S_B^\circ - S_B^s)$ is the entropy of vaporisation of the liquid solvent. For a large number of solvents $\frac{(S_B^\circ - S_B^s)}{R} \sim -8$

to -7 , and hence if $\log \frac{1.7\Delta}{M} 10^7 \sim 5$ $\log \frac{Z'}{Z} \sim 3$ to 2 .

There are cases of reactions in which the collision number in solution has been found to be equal to that in the gas phase. Such an agreement should be considered as arising from the fortuitous cancellation of the entropy terms in equation (34). In the units in which S is expressed in (34b) this cancellation occurs when the algebraic sum of the S 's approximately equals 5. If we assume that our present knowledge of the range of S , which is presented in Fig. 3, gives us a fair estimate of the possible magnitudes of this quantity for the reactants as well as for transition states then we see that there is some probability of observing the same collision number in solution and in the gas phase, since the values of S/R range from 5 to 10 and obviously the quantity $\left(\frac{S_T}{R} - \frac{S_A}{R} - \frac{S_B}{R}\right)$ has a considerable likelihood of being about 5 if each of the three terms lies within the range 5 to 10.

One case, however, stands out in which the agreement of the collision number in solution and in the gas phase seems to be based on a principle; it is the number of collisions between H_2 and O_2 measured by the magnetic conversion rate of parahydrogen, which has been found to be equal in the gas phase and in aqueous solutions.²⁰ This is a purely

¹⁹ The extent to which a solvent is known to influence a collision number in some cases of "slow" reactions shows that we might expect the range of S to be greater in these cases than shown in Fig. 3.

²⁰ L. Farkas and H. Sachse, *Z. physik. Chem., B*, 1933, 23, 1; 1933, 23, 19.

"physical" collision in which the collided state is completely defined by a certain range of distances between the interacting particles; there is no fusion into a compound as represented by the transition state of a chemical reaction. The entropy of solution of a pair of gas molecule is naturally independent of their distance so long as this distance is considerable. This independence may hold even at small distances as it apparently does in aqueous solutions of H_2 and O_2 . It seems improbable, however, that this should be generally so in all solvents.

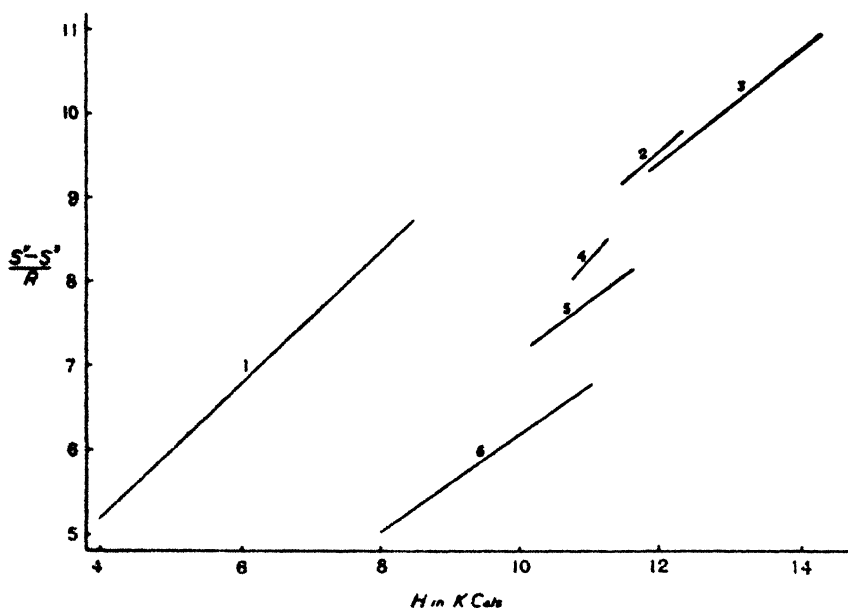


FIG. 3.—Key to Solutes.—1. Benzene; 2. Phenol; 3. Phenanthrene, 4. Nitrobenzene; 5. Naphthalene, 6. Benzoic acid.

If $K_1, K_2 \dots K_j \dots$ are the equilibrium constants for a reaction $n_A A + n_B B \dots = \nu_a a + \nu_b b \dots$ in a series of solvents 1, 2, 3 $\dots j \dots$ then K_1 and K_j are related by

$$\sum_A n_A \log X_i^A - \sum_a \nu_a \log X_i^a - \sum_A n_A \log X_j^A + \sum_a \nu_a \log X_j^a + \log K^i - \log K^j = 0. \quad (35)$$

But $\log X_i^A = -\frac{H_i^A}{RT} + \frac{S_i^A}{R}$ and similar equations hold for the reactants B \dots and a, b \dots for solvent i as well as for solvent j . Moreover, from equation (32) we have $\frac{S_i^A}{R} = \rho_A H_i^A + \text{const.}$ for all values of A and $i = i$ or j .

Therefore, equation (34) becomes

$$\begin{aligned} \frac{1}{RT} \sum_A n_A (H_j^A - H_i^A) - \frac{1}{RT} \sum_a \nu_a (H_j^a - H_i^a) - \sum_A \rho_A n_A (H_j^A - H_i^A) \\ + \sum_a \rho_a \nu_a (H_j^a - H_i^a) + \log K^i - \log K^j = 0. \quad (36) \end{aligned}$$

If the equilibrium constant K_i the reaction heat H_i and the heats of solution of the reactants A, B . . . a, b . . . are known for *one* solvent i , the equilibrium constant in any other solvent j can be calculated from a knowledge of the reaction heat, the heats of solution of the reactants, A, B . . . a, b . . . in that solvent and of the constants $\rho_A, \rho_B, \dots \rho_a, \rho_b, \dots$. The application of this theorem to ordinary equilibria is perhaps of little interest, but the analogous conclusion to be drawn for the equilibrium between the initial and the transition states seems to offer a rational approach to the study of solvent influence on reaction velocity.

Starting with a knowledge of the velocity constants k_i and k_j , the activation energies Q_i and Q_j , the heats of solution of the reactants H_i^A and H_j^A in the two solvents i and j and a knowledge of the constants ρ_A, ρ_B, \dots we can calculate the ρ constant for the transition state ρ_r .

$$\frac{1}{RT} \sum_A n_A (H_j^A - H_i^A) - \frac{1}{RT} (H_j^r - H_i^r) - \sum_A \rho_A n_A (H_j^A - H_i^A) + \rho_r (H_j^r - H_i^r) + \log k_i - \log k_j = 0.$$

We can now calculate the reaction velocity constant in any solvent provided that we know the activation energy and the heat of solution of the reactants in that solvent.

$$\log Z_j = - \sum_A \rho_A n_A (H_j^A - H_i^A) + \rho_r (H_j^r - H_i^r - Q_i + Q_j) + \log Z_i. \quad (37)$$

That is, we predict the relationship between the activation energy and the temperature independent factor Z in any solvent from solubility data and preliminary kinetic measurements in two solvents.

There are no sufficient data at present to test this relationship. We can only emphasise that this equation must hold if ρ_r exists; that is, the transition state behaves like other solute non-electrolyte substances reviewed in the previous section.

Referring once more to the discussion on page 1349, we note that if the two reactants and the transition state as solutes all behave like benzene, we might expect the change of solvent to cause variations of collision number of the order of 10^3 which would be accompanied by a change of 5000 cal. in the activation energy.

The variations in the entropy of solution offer a possible explanation for the fact that in some cases the temperature independent factor of monomolecular reactions deviates from the theoretical value of 10^{13} . Whereas lesser values than 10^{13} could be attributed to deviations from the classical dynamics assumed in the derivation of this factor,²¹ greater values could not be hitherto explained, except where chain reactions are present. We see now that such deviations might be due to an increase in the entropy of solution accompanying the change from the initial state to the transition state.

An analogous consideration might be applied to the monomolecular changes of large molecules in general, including the gas phase. Instead of the sheath of solvent molecules causing a variation of entropy we might in this case imagine the constituent parts of the reacting molecule to adopt the same rôle. Such considerations would constitute an extension of the theory of Polanyi and Wigner²¹ who, in their calculation of the

²¹ *Z. physik. Chem., Haber Band*, 1928, 439.

probability of the transition state have restricted themselves to the consideration of one-, two- or three-dimensional elongation of one bond.

8. Continuous Changes of the Solvent.

The addition of electrolytes or non-electrolytes which do not participate in the reaction, as well as the progressive replacement of the solvent by another perfectly miscible solvent can obviously be treated on the same lines as the discontinuous change through a series of solvents. An indication of this has been given in Section 3. There is not enough experimental material to justify a further discussion at the moment.

9. The Influence of Viscosity on Bimolecular Reaction Rate in Solution.

Various authors have tried to correlate collision numbers to the viscosity of the medium, whereas viscosity does not enter into our theory. Now it is obvious that if the viscosity of the medium were to assume very high values, *e.g.* when the solvent passes into the vitreous state, bimolecular reactions would necessarily be slowed down almost to zero rates. Nevertheless, it can be shown that for ordinary liquids the influence of viscosity on collision number is negligible.

In our application of the transition state method we have assumed that every "representative point" passing the transition state in either direction should lead to a completion of the reaction in that direction. That is, if two particles are formed in the reaction these should be dissipated in the solution. Otherwise, if they stick together, they would have a greater tendency to enter with each other into a back reaction than has an average pair of neighbouring molecules, and the reaction could not be regarded as being fully completed.

The tendency for the newly formed particles to stick together increases with the viscosity of the solution. The effect of the viscosity becomes noticeable when two particles existing in the collided state move away so slowly from each other that they enter the back reaction before they have time to get away to a distance corresponding to the average distance of the solute molecules.

It follows that under ordinary conditions the viscosity has no influence on the collision number. Assuming, *e.g.*, an activation energy of 18,000 cal., two collided particles would react at ordinary temperatures in the course of 1 second, while in a molar solution the time required to diffuse over a distance corresponding to the average separation of the molecules, *i.e.* about $1 \cdot 10^{-7}$ cm., would be about $3 \cdot 10^{-4}$ sec. if the diffusion constant is of the order of 1 day/cm^2 . On the other hand it is clear that if the viscosity reaches 10^7 -times as high values (so that the diffusion constant becomes of the order of 10^7 day/cm^2 which would correspond to a vitreous state), the times of reaction and diffusion would become comparable and the latter would even become greater than the former. Under these conditions the diffusion of the particles would become the rate determining factors and the rate of the (inverse) bimolecular reaction would become independent of the activation energy and inversely proportional to the viscosity. Small activation energies of the reaction and great dilution would favour this state of affairs.

The reactions with small activation energies which are impeded by small steric factors would require a slightly different treatment which we do not wish to discuss at this stage. It is, however, easy to see that the hindrance caused by a steric factor might be taken as approximately equivalent to that caused by an activation energy.

10. Relationships of Energy and Entropy Based on the Nernst Theorem.

For a more detailed understanding of this relationship we first consider conditions at $T = 0$. According to the Nernst theorem we have

$$\left(\frac{\partial S}{\partial \chi}\right)_{T=0} = 0,$$

$$RT\left(\frac{\partial \log K}{\partial \chi}\right)_{T=0} = (\beta_1 - \beta_2)^0 = -\left(\frac{\partial H}{\partial \chi}\right)_{T=0}.$$

Assuming $(\beta_1 - \beta_2)^0 = \text{const.}$, we obtain for $RT \log K$ and H as functions of χ two straight lines at equal and opposite angles (Fig. 4), whereas TS is a horizontal.

For finite temperatures we have

$$RT\left(\frac{\partial \log K}{\partial \chi}\right)_T = (\beta_1 - \beta_2)^0 + \int_0^T \left(\frac{\partial(\beta_1 - \beta_2)}{\partial T}\right)_\chi dT, \quad (38)$$

$$-\left(\frac{\partial H}{\partial \chi}\right)_T = (\beta_1 - \beta_2)^0 + \int_0^T \left(\frac{\partial(\beta_1 - \beta_2)}{\partial T}\right)_\chi dT - T\left(\frac{\partial(\beta_1 - \beta_2)}{\partial T}\right)_\chi, \quad (39)$$

$$T\frac{\partial S}{\partial \chi} = T\left(\frac{\partial(\beta_1 - \beta_2)}{\partial T}\right)_\chi. \quad (40)$$

and after integration

$$RT \log K = (\beta_1 - \beta_2)^0 \chi + \chi \int_0^T \left(\frac{\partial(\beta_1 - \beta_2)}{\partial T}\right)_\chi dT + \text{const.} \quad (41)$$

$$-H = (\beta_1 - \beta_2)^0 \chi + \chi \int_0^T \left(\frac{\partial(\beta_1 - \beta_2)}{\partial T}\right)_\chi dT - \chi T\left(\frac{\partial(\beta_1 - \beta_2)}{\partial T}\right)_\chi + \text{const.} \quad (42)$$

$$TS = \chi T\left(\frac{\partial(\beta_1 - \beta_2)}{\partial T}\right)_\chi + \text{const.} \quad (43)$$

The magnitude of the coefficients of χ arising from the elevation of temperature are defined graphically in Fig. 4. under the probable assumption that $(\beta_1 - \beta_2)$ changes monotonously with temperature. The Fig. 5 shows that we might expect the sequence

$$T\left(\frac{\partial(\beta_1 - \beta_2)}{\partial T}\right)_\chi > \left\{ \int_0^T \left(\frac{\partial(\beta_1 - \beta_2)}{\partial T}\right)_\chi dT - T\left(\frac{\partial(\beta_1 - \beta_2)}{\partial T}\right)_\chi \right\} \\ > \int_0^T \left(\frac{\partial(\beta_1 - \beta_2)}{\partial T}\right)_\chi dT. \quad (44)$$

All three lines representing $RT \ln k$, H and TS are seen to change their inclinations with increasing temperature in the same direction, the magnitude of the change being greatest for the TS line and smallest for the $RT \ln k$ line. The two possible cases are a *decrease* or an *increase* of the angles with temperature, corresponding to whether $\beta_1 - \beta_2$ increases or decreases with temperature. We have for Case I

$$-\left(\frac{\partial H}{\partial \chi}\right)^0 > 0; \left\{ \int_0^T \frac{\partial(\beta_1 - \beta_2)}{\partial T} dT - T \frac{\partial(\beta_1 - \beta_2)}{\partial T} \right\} < 0,$$

$$\text{i.e. } \int_0^T T \frac{\partial^2(\beta_1 - \beta_2)}{\partial T^2} dT > 0 \quad (45)$$

or the same inequalities with the opposite sign throughout, and for Case II

$$-\left(\frac{\partial H}{\partial \chi}\right)^0 > 0; \left\{ \int_0^T \frac{\partial(\beta_1 - \beta_2)}{\partial T} dT - T \frac{\partial(\beta_1 - \beta_2)}{\partial T} \right\} > 0;$$

$$\text{i.e. } \int_0^T T \frac{\partial^2(\beta_1 - \beta_2)}{\partial T^2} dT < 0 \quad (46)$$

or the same inequalities with the opposite sign throughout. As an alternative characteristic of the two cases we can introduce the influence

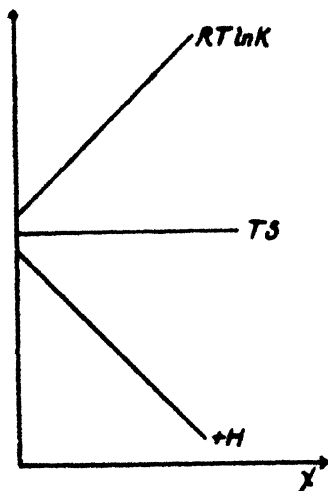


FIG. 4.

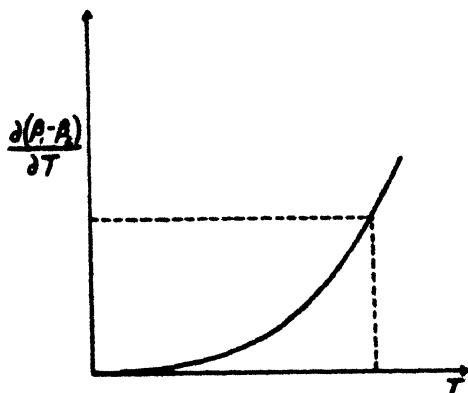


FIG. 5.

of χ on the difference of heat capacities at constant χ , $(c_1 - c_2)$ between states 1 and 2. Thus we have Case I or Case II according to whether the sign of $-\left(\frac{\partial H}{\partial \chi}\right)$ is opposite or equal to that of $\int \frac{\partial(c_1 - c_2)}{\partial \chi} dT$.

Applying these considerations to reaction velocities,²² we obtain the following features of the two cases.

Starting from $T = 0$ and increasing the temperature, Case I exhibits two phases which are shown in Figs. 6 and 7. In Phase 1 the change of activation energy which is of opposite sign to the change of the velocity constant and of the temperature independent factor, the variations of the activation energy and the temp. ind. factor thus supplementing each other in determining the change of velocity constant. Such a complementary relationship is excluded in Case II.

²² Our deductions actually refer to the equilibrium constant K between the initial and the transition states; the velocity constant is related to this by the equation $k = \frac{1}{h} K v$.

(see Fig. 8) where the variations of activation energy and temperature independent factor always oppose each other.

In Phase 2 of Case I. which is reached at more elevated temperatures when

$$\left\{ \int \frac{\partial(\beta_1 - \beta_2)}{\partial T} dT - T \frac{\partial(\beta_1 - \beta_2)}{\partial T} \right\} < (\beta_1 - \beta_2)^0$$

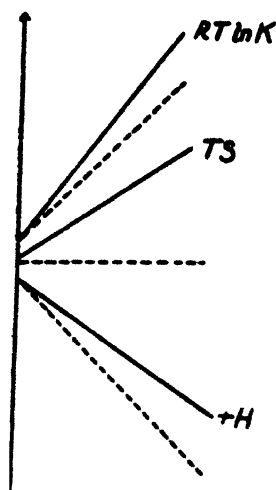


FIG. 6.

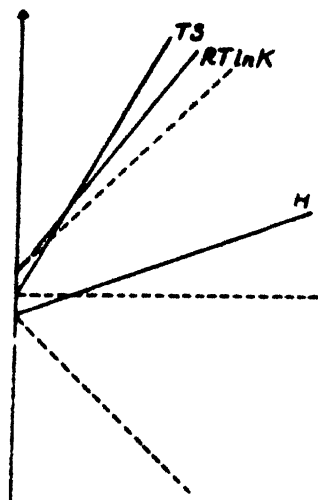


FIG. 7.

causes $-(dH/dX)$ to pass through zero, we have equal sign in the change of activation energy and temperature independent factor so that these

two effects oppose each other in their influence on the reaction velocity. In this opposition the temperature independent factor prevails, so that the sign of its variations governs the sign in which reaction velocity changes. We shall see that this is not so when an opposition of the same two factors is present in Case II.

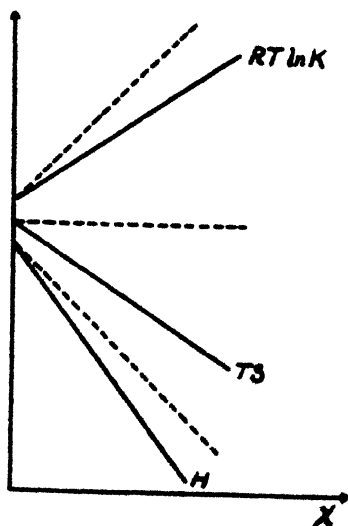


FIG. 8.

A sequence of reaction velocities belongs to Case II. if the changes in activation energy and temperature independent factor are of equal sign, *i.e.*, in effect oppose each other and the activation energy predominates so that its trend governs the change of reaction velocity.

The only example we know for Case I. is the effect of hydrostatic pressure on the reaction between pyridine and ethyliodide in acetone and between acetic anhydride and ethyl alcohol in toluene solution. Both the activation energy and the collision number of these reactions are in-

creased by pressure, the latter factor being predominant. This corresponds to Phase 2 of Case I.

All other reactions measured under the influence of hydrostatic pressure show the characteristics of Case II. So do all the reactions discussed in Section 5. We observe the same characteristics in the solvent-solute equilibria surveyed in Section 6; all the variations in heats and the entropies of solution oppose each other in their effects on solubility and the energy variation predominates in governing the solubility.

The following considerations suggest that Case I. is likely to be realised when χ is an external force while Case II. is present when χ is a force intrinsic to the reacting system.

As an example for the effect of external forces we consider the hydrostatic pressure. Supposing the reaction proceeds in the direction of smaller molar volume, we have $-(\partial H/\partial \chi) > 0$ at low temperatures. Such a reaction being accompanied by contraction will generally lead to a reduction of the expansion coefficient and also of its differential $\partial^2 V/\partial T^2$ with respect to temperature. It follows since

$$\int T \frac{\partial^2 V}{\partial T^2} dT = - \int \frac{\partial C}{\partial \chi} dT$$

that reactions which lead to contraction reduce the pressure dependence of the heat capacity. Hydrostatic pressure will, therefore, reduce the heat capacity of the initial state to a greater extent than that of the final or transition state, thus fulfilling the conditions of Case I.

This conclusion, however, holds only if changes in volume and in the temperature coefficients of thermal expansion change in the same direction. This certainly does not hold for associating solvents which might explain that the numerous reactions measured under hydrostatic pressure in alcoholic solutions do not conform to Case I.

Now let χ be a measure of the attractive forces (intrinsic parameter) between the atoms taking part in the reaction leading from state 1 to state 2. Then $-(\partial H/\partial \chi) > 0$ if the forces χ are greater in 2 than in 1.

For a system of n quasi-elastic oscillators of equal frequency ν the specific heat can be expressed in terms of frequencies.

$$\frac{C}{R} = \left(\frac{h\nu}{kT} \right)^2 \frac{\exp \left(\frac{h\nu}{kT} \right)}{\left(\exp \left(\frac{h\nu}{kT} \right) - 1 \right)^2}$$

An increase of the force constants tends to increase the ν -values and hence to decrease the specific heat. According to the assumption made in the foregoing paragraph this decrease is greater for state 2 than state 1 if $-(\partial H/\partial \chi) > 0$. Hence $\frac{\partial(c_1 - c_2)}{\partial \chi} > 0$, i.e., we have an opposing sign in the variation of H and $C_1 - C_2$ with χ which is characteristic of Case II.

We expect, therefore, Case II. to hold whenever variations of equilibrium or reaction rates are governed by changes in the nature of the reacting system. The reacting system naturally including solvent molecules.

As already pointed out a moment ago, Case II. is actually found to hold all over the field of linear relationships surveyed in this paper where the nature of the reacting system varies by changes in intrinsic forces.

To this material we might add, following a survey by Moelwyn-Hughes,²³ various observations which point in the same direction although not always conforming strictly to the linear relationship. Thus Boeseken²⁴ finds that the velocity constant of many reactions can be expressed $k = Je^{Q/C}e^{-Q/RT}$ where J and C are constants. Although this formulation implies a linear relationship between the temperature independent factor and the activation energy the agreement is only qualitative.

The above equation has been shown to apply to surface catalytic reactions²⁵ where the constant C is characteristic of the catalyst, and by Syrkin²⁷ to unimolecular reactions.

There is also evidence that for such parts of an adsorbing surface which exert high attraction forces the temperature independent factor is the smaller the higher the adsorption potential, the two factors thus counteracting each other in their effect on the adsorption equilibrium.²⁸ The extremely small values to which the entropy factor has been found to go down at high adsorption potentials is remarkable. A similar and probably essentially related phenomenon is observed in the kinetics of slow (activated) adsorption, the temperature independent factor being found to have abnormally low values.²⁹

Although the preceding survey shows clearly that the natural variations of chemical systems do very often conform to Case II. we hesitate at this stage to lay down definitely that all such natural variations must conform to Case II. The atomic picture which we used for the deduction of this theorem is not general enough to justify more than the expectation that the characteristics of Case II. will hold as a rule, while it also indicates on what lines possible exceptions to this rule might be explained.

11. Relevance of Activation Energies Derived from Energy Surfaces.

The considerations of the present section should make it clear to what extent calculations of the sequence of activation energies derived from atomic mechanism can be legitimately applied to kinetic data at ordinary temperatures. The values of $\log k$ will always follow the trend derived for the activation energies at $T = 0$, whereas the observed activation energies can follow an opposite trend to that calculated at $T = 0$, e.g. when hydrostatic pressure causes an increase in activation energy (Phase 2 of Case I.).

The inequalities (45) and (46) also show that of the three quantities $\log k$, Q and TS , the coefficient of χ arising from increase of temperature is the smallest in the expression of $\log k$. So even when the observed Q

²³ Moelwyn-Hughes, *Kinetics of Reaction in Solution*, Oxford University Press, 1933, p. 167.

²⁴ *Rec. Trav. Chim.*, 1927, **46**, 574.

²⁵ Holdzschmidt, *Z. anorg. Chem.*, 1931, **200**, 82.

²⁶ G. M. Schwab, *Z. physik. Chem., B*, 1929, **5**, 406.

²⁷ *Z. anorg. Chem.*, 1931, **199**, 28.

²⁸ Polanyi and Welke, *Z. physik. Chem., A*, 1928, **132**, 371.

²⁹ H. S. Taylor, *Trans. Faraday Soc.*, 1932, **28**, 137.

and $\log k$ both change with χ in the same direction as they would at $T = 0$, it is the trend of $\log k$ (and not of Q) which gives the better approximation to the change of Q with χ as calculated for $T = 0$.

Since the trend of $\log k$ derived for $T = 0$ is not changed in sign by raising the temperature, we can understand that the theorem relating heats of reaction to reaction velocities and the subsequently developed theory of Bronsted's equation, as well as that of the closely related Tafel equation, which were all based on calculations referring implicitly to $T = 0$ were found to conform satisfactorily to reaction rates measured at ordinary temperatures. It is also apparent that the *activation energies* measured at ordinary temperatures will be less likely to follow the trend derived for $T = 0$ and that it is quite improbable that the activation energies of reactions occurring in solutions should, at ordinary temperatures, reflect quantitatively the results derived for $T = 0$.

This removes the difficulty to the theory of acid base catalysis recently pointed out by Bell³⁰ (who has, himself, developed an alternative form of the theory of Horiuti and Polanyi) consisting in the fact that the activation energies accompanying the variable rates are almost constant. Although this is no objection to the semi-quantitative side of the theory which for ordinary temperatures requires only parallelism between $\log k$ and $\log K$, it does, nevertheless, indicate that the quantitative results of the theory require qualification corresponding to the difference between $T = 0$ and ordinary temperatures.

Summary.

The following are the main points of the present study.

1. Deduction of the laws of thermodynamics for the isothermic change of a parameter χ operating on the chemical equilibrium or on the rate of a reaction. The main example for testing these laws is the case when χ is the hydrostatic pressure. While the Arrhenius equation yields the energy and specific heat of the transition state, we can also measure the volume, the heat expansion and the compressibility of a solution of the transition state from kinetic measurements under hydrostatic pressure.

2. Extension of the scope of thermodynamics by assuming that χ might represent the intensity of a molecular field. Although we cannot measure these intensities the laws thus derived can be tested, if it is assumed that for corresponding members (i or j) of two analogous sets of reactions A and B the values of χ are identical, i.e., $x_i^A = x_i^B$; $x_j^A = x_j^B$ or that at least

$$\frac{x_i^A}{x_i^B} = \frac{x_j^A}{x_j^B} = \text{const.}$$

We can then eliminate χ . Assuming further that the linear terms of the integrated isotherm offer a satisfactory approximation over an extended range of χ we obtain a linear relationship between values of chemical free energies $RT \log K^A$, $RT \log K^B$. . . $RT \log k^A$, $RT \log k^B$. . . reaction heats H^A , H^B . . . activation energies Q^A , Q^B . . ., in all possible combinations of these magnitudes.

3. The experimental material conforming to these relationships is ample. To this we have added one new example. We found that a linear relationship holds between the free energy of solution and the heat of solution for a given non-electrolyte solute in different solvents. A similar relationship holds for chemically related substances when different solutes are taken in the same solvent.

³⁰ *Proc. Roy. Soc., A*, 1936, **154**, 414.

4. These results have been used as an empirical framework in which to restate our previous theory of collision number in solution, and to particularise the conditions under which it will be greater or smaller than the collision number in the gas phase. We also conclude that from kinetic measurements made in two solvents and from solubility data the collision number for any other solvent can be predicted if the activation energy in that solvent is known. We have also discussed the influence of viscosity on bimolecular reaction rates and found it to be negligible.

5. The influence of a variable χ on the reaction rate can be approximately predicted from the influence it exercises on the equilibrium, whenever the derivatives of the free energy and the energy with respect to χ relating to the transition state lie intermediate between those relating to the initial and final states. An example can be fully worked out for verification in case that χ is the hydrostatic pressure. For Bronsted's law of acid base catalysis and Tafel's overvoltage equation the new treatment shows that the previous theory applies strictly only to $T = 0$ and indicates the lines on which this theory should be revised.

6. The coefficients of χ in the integrated isotherm have been determined by use of the Nernst theorem. It follows that under the influence of χ entropies and energies can vary according to two different types (Case I. and Case II. characterised by equations (45) and (46) respectively). An explanation is given for the fact that Case I. is only fulfilled when χ is the hydrostatic pressure and Case II. is present when χ is a force intrinsic to the reacting system of the sort which determines the natural variations of chemical properties. The main feature of Case II. is the opposing influence in the variations of the activation energy and the collision number which is observed in many series of chemical reactions and the analogous opposition in the variations of heat and entropy on the solubility of a solute in different solvents.

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THE OSMOTIC PRESSURE OF GUM ARABIC.

PART II.—THE "MOLECULAR WEIGHT" WITH DIFFERENT BASES.

BY HENRY BOWEN OAKLEY.

Received 19th May, 1936.

In the following paper, which amplifies the preliminary work reported in 1934,¹ an attempt has been made to find out whether compounds of the gum with different bases have the same mean particle size or "molecular weight." This involves making sure that the part of the osmotic pressure due to the metallic cations of the gum is entirely eliminated. This has been accomplished by making measurements at low concentrations in solutions of the chloride of the appropriate base at a concentration sufficient to eliminate the ionic pressure in accordance with the theory of the Donnan² membrane equilibrium.

It is shown in a subsequent paper (Part III.)* that the osmotic pressure of the colloid particles is only about 1 per cent. of the total

¹ H. B. Oakley, *Trans. Faraday Soc.*, 1935, **31**, 136.

² F. G. Donnan, *ibid.*, 82, and discussion by G. S. Hartley, 1935, p. 107.

* To be published shortly.

osmotic pressure of the gum plus its cations as measured against pure water, so that, even if 99.9 per cent. of the ionic pressure has been eliminated, the remaining osmotic pressure will still be 10 per cent. higher than the true value for the colloid particles alone.

Preparation of Specimens of Gum.

An improvement in preparation has been introduced by following the precautions described by L. Amy,³ who showed that Gum Arabic contains an insoluble gelatinous constituent which is, however, easily peptised by a solution of gum. All gum solutions were, therefore, prepared by spreading the powdered gum on a filter paper suspended horizontally on a wire gauze and just touching the surface of water in a beaker. In a few days all the gum dissolved leaving behind about 0.1 per cent. of gelatinous constituent. Precipitation with alcohol was avoided as the above author maintains that this treatment tends to increase the insoluble fraction which may, however, still be peptised in gum solution but which cannot be removed by dialysis. About 5 per cent. solutions prepared as above, after sterilising in a water-bath for 20 minutes, were dialysed in collodion sacs against many changes of $N/2$ solutions of the chloride of the respective bases. Silver nitrate was used for the silver gum, but in this case a preliminary dialysis against sodium nitrate was made and in this way no reduced silver was produced even after two or three weeks. Thymol was added in all cases. Such preparations showed no reduction of Fehling's solution.

With some later experiments on sodium and calcium gums, some comparative measurements were also made on specimens prepared by neutralising electro-dialysed gum. As pointed out by the present author¹ and confirmed by Amy,³ the acid gum (unlike the neutral gum) is not stable. The later stages of the electrodialysis were, therefore, carried out in well-cooled solutions and the gum neutralised immediately the dialysis was finished.³

In all cases the gum solutions were finally dialysed against portions of the same salt solution that was to be employed in the osmometer, so that diffusible impurities were removed and the salt equilibrium already established before introduction into the osmometer.

The concentration of the gum was estimated by withdrawing the solution from the osmometer and drying *in vacuo* at 100° and subtracting the appropriate weight of salt, it being assumed that the concentration of the salt relative to the water at low concentrations of the gum was the same on both sides of the membrane.

The special low-pressure osmometer described previously¹ has been slightly modified for greater convenience and accuracy, as reported in a recent publication on glycogen,⁴ special attention being paid to temperature control to less than 0.01°. All measurements were made at 25°, 20 hours being allowed in most cases for equilibrium to be established.

Sodium Gum.

In Fig. 1 P/C is plotted against C for five concentrations of NaCl; where P = osmotic pressure in mm. water and C = concentration in grams of gum per 100 grams of water. Circles represent results for gum which had not been electro-dialysed and crosses those for electro-dialysed gum subsequently neutralised with NaOH (or Ca(OH)₂); they are in good agreement. The experimental error below a concentration of 0.3 per cent. becomes large, *i.e.*, over 10 per cent.

³ L. Amy, *Annales de Chimie*, 1934, 2, 295.

⁴ H. B. Oakley, F. G. Young, in press, *Biochem. Jour.*, 1936.

From the lower experimental error obtained with glycogen⁴ it would appear that this error is to be attributed not entirely to the osmotic pressure

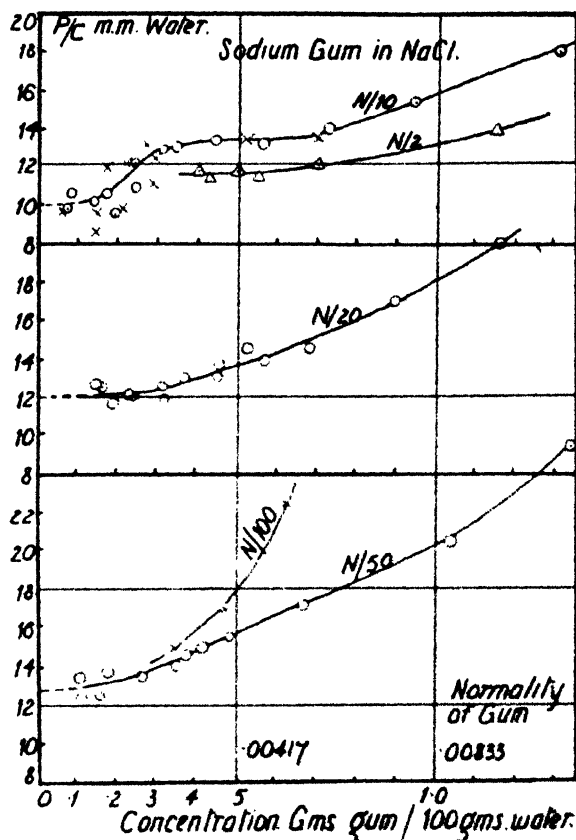


FIG. 1.

for P/C of about 13, and subsequently appears to drop to a value of 10, unless this is to be rejected as experimental error. With $N/2$ NaCl the

measurements but, in part, to some inherent difficulty in obtaining reproducibility of equilibrium with the gum, and in part, to errors in the estimation of concentration, due to the small weight of gum present (20 or 30 mg.) with the much larger weight of salt. The osmotic pressure in these dilute regions amounts to only 1.0 to 2.5 mm.

The results for $N/50$ and $N/20$ NaCl show that these concentrations are insufficient to suppress the ionic pressure difference at a concentration of gum high enough for accurate measurement, although a limiting value of 12 to 13 appears to be approached.

The curve for $N/10$ NaCl shows a marked flattening, between concentrations of 0.7 and 0.3 per cent., to a value

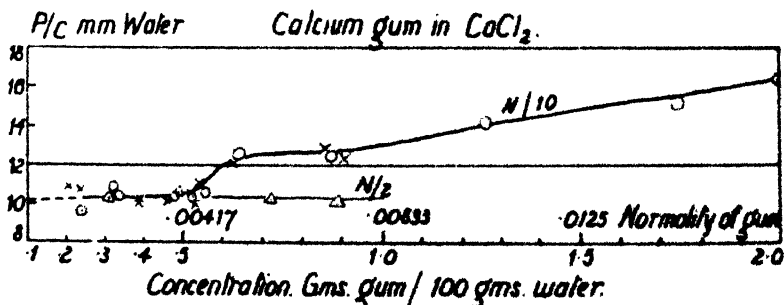


FIG. 2.

curve flattens to a value for P/C of 11.6; values at concentrations below 0.4 per cent. were not obtained, the error of weighing such small quantities of gum may be expected to increase with the amount of NaCl present.

Calcium Gum.

Fig. 2 gives similar results for two concentrations of calcium chloride with calcium gum. This curve for $N/10$ CaCl_2 , again appears to show an initial flattening to a value of 12.6 followed by a sharp fall to about 10. It will be seen that this is confirmed by several repetitions of experimental points. These regions occur at higher concentrations than is the case with sodium gum. With $N/2$ CaCl_2 , the value of P/C is constant at 10.3 between concentrations of 0.3 to 0.9 per cent. of gum. The implication of these results will be discussed later.

Comparison of Gums with Different Bases.

Before these results had been obtained experiments were made with silver, lead, potassium, lithium, sodium and calcium gums at concentrations not lower than 0.3 per cent. The concentrations of the alkali chlorides were $N/2$, that of silver nitrate $N/10$, and of lead nitrate $N/5$. The results are shown in Table I. Those for sodium and calcium have already been included in Figs. 1 and 2. P is expressed in mm. of water.

Too much reliance cannot be placed on the figures for silver, lead and lithium gums owing to the possibility of decomposition or partial hydration of the salts with the drying technique employed. The mean values for P/C would correspond to the initial flattening of the curve described previously, and while five of the compounds agree within 10 per cent. of each other with a value of about 11.7 the calcium gives a lower figure of 10.3.

Discussion.

If for the moment all results below 0.3 per cent. of gum are neglected the figures given in Table II. are obtained for the limiting value of P/C and the molecular weight under different conditions. M was calculated from the equation $M = 10 RT \cdot C/P = 2.52 \times 10^6 \times C/P$ at 25° , where P is expressed in mm. of water.

The figures for sodium gum differ from those reported in the preliminary investigation¹ where the non-electro-dialysed gum gave a value of 152,000 and the electro-dialysed gum one of 245,000. The differences are attributed to the modified mode of preparation and to the fact that the present samples were kept in dialysers instead of in bottles. The agreement between electro-dialysed and non-electro-dialysed samples is considered to be good evidence that the present figures are reliable.

TABLE I.

C.	P.	P/C.	C.	P.	P/C.
Silver gum ($N/10$ AgNO_3).			Lead gum ($N/2$ $\text{Pb}(\text{NO}_3)_2$).		
0.35	4.0	11.4	0.29	3.3	11.4
0.47	0.1	13.0	0.35	4.2	12.0
0.57	6.7	11.8	0.60	7.7	11.7
0.79	9.0	12.0			
Mean = 12.0			Mean = 11.7		
Sodium gum ($N/5$ NaCl).			Potassium gum ($N/2$ KCl).		
0.40	4.7	11.8	0.30	3.4	11.3
0.43	4.9	11.4	0.41	4.5	11.0
0.50	5.9	11.8	0.50	6.5	11.6
0.55	6.3	11.5	0.80	10.1	11.4
0.70	8.5	12.1*	1.10	13.0	11.8*
1.15	16.0	13.9*	1.55	21.7	14.0*
Mean = 11.6			Mean = 11.3		
Lithium gum ($N/2$ LiCl).			Calcium gum ($N/2$ CaCl_2).		
0.37	4.4	11.9	0.31	3.2	10.3
0.51	6.3	12.0	0.49	5.2	10.6
0.60	9.2	13.4*	0.72	7.4	10.3
1.13	14.7	13.0*	0.88	9.0	10.2
Mean = 12.2			Mean = 10.3		

* These results were not included in the averages.

TABLE II.

Salt.	Concentration.	P/C .	M .	
NaCl . .	$N/10$	13.3	191,000	± 2.2 per cent.
	$N/2$	11.6	217,000	± 1.5 " "
KCl . .	$N/2$	11.3	224,000	± 2 " "
CaCl ₂ . .	$N/10$	10.3	245,000	± 2 " "
	$N/2$	10.3	245,000	± 2 " "
LiCl . .	$N/2$	12.2	206,000	± 3 " "
Pb(NO ₃) ₂ . .	$N/8$	11.7	215,000	± 2 " "
AgNO ₃ . .	$N/10$	12.0	210,000	± 6 " "

The increase of molecular weight with increasing NaCl concentration or the higher value in the case of calcium chloride would then be attributed either to increasing aggregation of a single molecular species of gum, or to aggregation of a small quantity of a substance of lower molecular weight. In neither case does this explain the rise of P/C in $N/10$ CaCl₂ to a second level of 12.6.

If the above explanation is adopted, then this singularity and the falling values of P/C in $N/10$ NaCl below a concentration of 0.3 per cent. must be dismissed as experimental error.

If, however, these values are accepted it becomes necessary to account for the sudden fall in osmotic pressure at extremely high dilutions.

The ultracentrifuge would be the only means for obtaining accurate data at such high dilutions, and until further data have been obtained it would appear unprofitable to discuss the matter further. The fact that osmotic data for proteins agree with those obtained at high dilutions by the ultracentrifuge does not necessarily mean that this would also be the case for the very highly charged particles of gum.

Summary.

1. From osmotic pressure measurements down to a concentration of 0.3 per cent. of gum a mean particle weight of 220,000 ± 10 per cent. has been obtained for Li, Na, K, Ag and Pb gum arabic salts in $N/2$ solutions of the alkali chlorides and $N/10$ AgNO₃ and $N/5$ Pb(NO₃)₂.

2. With NaCl the weight in $N/10$ and $N/2$ solutions was 191,000 ± 2.2 per cent. and 217,000 ± 1.5 per cent. respectively.

3. With CaCl₂ the weight was in both cases 245,000 ± 2 per cent.

4. Below concentrations of 0.3 per cent. the particle weight of Na gum in $N/10$ NaCl appears to rise to 245,000 at 0.15 per cent. It is thought that measurements of such small osmotic pressures ought to be confirmed by the ultra-centrifuge before they can be discussed profitably.

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SIMPLE NUMERICAL RELATIONSHIPS IN BINARY EUTECTIC MIXTURES.

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In a recent paper¹ it has been shown that in eutectics containing two metals there is a reasonable probability that the atoms are present in a comparatively simple numerical ratio. These ratios range from 1 : 2 and 2 : 3 in the case of the simple cadmium-tin and copper-silver eutectics to 4 : 19 and 8 : 47 for the more complicated copper-aluminium and copper-magnesium systems, where the eutectics are between a primary and a secondary solid solution. This relationship has been put forward empirically solely as an expression of experimental results and theoretical reasons for its existence are not yet clear. If it is the effect of some method of fitting together the two kinds of molecules, it is perhaps to be expected that the more complicated the molecule, the more limited the possible ways of fit and the simpler the ratio. Other groups of binary eutectiferous systems : salt-water, two salts with a common ion, organic compounds, are therefore examined here.

The outstanding difficulty in such an examination is the choice of data. A casual glance at critical tables may give the impression that in a certain system the eutectic ratio is exactly 1 : 3, but reference to the original work may show that only some ten points on the two branches of the liquidus curves have been determined. That is, the eutectic composition has been found by considerable extrapolation. Further, on redrawing the original curves, it may be found possible to place the eutectic at anything between 23 and 27 molecular per cent. of one of the constituents and it may become obvious that the existing evidence in favour of its falling exactly at 25 per cent. is slender. In organic chemistry, particularly, there are almost too many data and it is only too easy, by making a non-critical selection, to prove either the existence or the non-existence of simple ratios. A statistical examination of a large number of systems gives general support to the idea of simple ratios, but this result is also unsatisfactory because of the large number of ratios which may be regarded as simple, together with the uncertainty of much of the experimental work and the fact that certain of the systems have been expressed in terms of molecular percentages, critical points being given in smoothed values, 25, 40, 50 per cent., as the case may be.

In certain cases, the accuracy demanded for the establishment of a rule is beyond present experimental skill. Thus, if the weight percentage of one of the constituents in the eutectic mixture is small it is usually impossible to decide definitely whether the ratio falls at 1 : 10 (9.09 mol. per cent.) or 2 : 21 (8.70 mol. per cent.), for example, or at something indeterminate in between. This effect is intensified if the molecular weight of the constituent present in least amount is much larger than that of the other. Thus, cryohydrates frequently contain a large percentage of water and the molecular weight of the salt

¹ Stockdale, *Proc. Roy. Soc., A*, 1935, 152, 81.

is often many times that of water. For these reasons, *pace* Guthrie, it seems to be impossible at present either to establish or to overthrow an empirical rule by evidence obtained from a study of salt-water mixtures, and such mixtures are not further considered here.

There remain eutectics containing two salts with a common ion and binary organic eutectics. Probably the most satisfactory method of obtaining evidence about these systems is to examine the work of a limited number of investigators who have between them determined the eutectic compositions in a considerable number of systems and to reject that of those who have evidently been unaware of the serious experimental difficulties which must be overcome before reliable results in determinations of this kind can be obtained. Having once chosen the investigators, *all* their results, except those which must be discarded for the reasons discussed under cryohydrates, must be presented.

W. M. Madgin and his colleagues have determined the eutectic compositions of nine binary nitrate systems in which the eutectic contains more than ten molecular percentages of each salt. Their results are used in Table I.

TABLE I.

System.		Molecular Percentage of A.	Ratio A : B.	Suggested Simple Ratio.	Weight Percentage of A Required by Ratio.	Weight Percentage of A Found by Experiment.	Difference Weight Percentage.
A	B						
Ca(NO ₃) ₂	NaNO ₃	33.41	1 : 1.99	1 : 2	49.11	49.2	0.1 ¹
Ba(NO ₃) ₂	KNO ₃	12.51	1 : 6.99	1 : 7	26.98	27.0	Nil ²
Sr(NO ₃) ₂	KNO ₃	48.33	1 : 1.07	—	—	66.2	— ²
Ca(NO ₃) ₂	KNO ₃	34.87	1 : 1.87	7 : 13	46.64	46.5	0.1 ²
Pb(NO ₃) ₂	KNO ₃	23.04	1 : 3.34	3 : 10	49.56	49.5	0.1 ⁴
Pb(NO ₃) ₂	NaNO ₃	15.84	1 : 5.31	3 : 16	42.21	42.3	0.1 ⁴
Pb(NO ₃) ₂	TiNO ₃	12.18	1 : 7.21	1 : 7	15.08	14.7	0.4 ⁵
Pb(NO ₃) ₂	NH ₄ NO ₃	10.43	1 : 8.59	—	—	32.5	— ⁶
KNO ₃	NH ₄ NO ₃	11.33	1 : 7.83	1 : 8	13.63	13.9	0.3 ⁶

The ratios given in Table I. are of the same nature as those found for metallic eutectics.⁷ For the metallic systems it has been shown that even though the ratios are sometimes so complicated that considered individually they are open to criticism, yet there is a definite probability that a simple ratio rule exists, and the present case appears to be parallel. The assessment of the results is rendered even more difficult by the impossibility at present of putting forward any other than an arbitrary definition of a simple ratio.

Two groups of binary organic eutectics are now considered. The first (Table II.) has been examined by Madgin and his colleagues, the second (Table III.) by N. A. Puschin and I. I. Rikovski.⁸ The latter work was undertaken to disprove a suggestion that the two branches

² K. Laybourn, W. M. Madgin and D. Freeman, *J. Chem. Soc.*, 1934, 139.

⁴ K. Laybourn and W. M. Madgin, *ibid.*, 1933, 236.

⁵ H. M. Glass, K. Laybourn and W. M. Madgin, *ibid.*, 1932, 874.

⁶ *Ibid.*⁴, 2713.

⁷ K. Laybourn, *Degree Thesis, Armstrong Collage, Newcastle-on-Tyne*, 1934.

⁸ *Ibid.*¹, pp. 96 and 99.

⁹ *Z. physik. Chem.*, A, 1930, 151, 257.

TABLE II.

System.		Molecular Percentage of A.	Ratio A : B.	Suggested Simple Ratio.	Weight Percentage of A Required by Ratio.	Weight Percentage of A Found by Experiment.	Difference Weight Percentage.
A	B						
<i>p</i> -Dichlorobenzene	<i>o</i> -Chlorophenol	17.94	1 : 4.57	2 : 9	20.26	20	0.26 ^o
<i>p</i> -Dichlorobenzene	Quinoline	11.15	1 : 7.97	1 : 8	12.46	12.5	0.04 ^o
Benzene	Quinoline	33.28	1 : 2.005	1 : 2	33.05	33	0.05 ^o
<i>p</i> -Dichlorobenzene	<i>p</i> -Toluidine	40.69	2 : 2.92	2 : 3	47.78	48.5	0.7 ¹⁰
<i>p</i> -Toluidine	Benzene	20.39	1 : 3.91	1 : 4	25.53	26	0.5 ¹⁰
<i>p</i> -Dichlorobenzene	<i>o</i> -Cresol	27.03	1 : 2.70	3 : 8	33.77	33.5	0.27 ¹⁰
<i>o</i> -Cresol	Benzene	32.04	1 : 2.12	—	—	39.5	— ¹⁰

TABLE III.

System.		Number.	Molecular Percentage of A.	Ratio A : B.	Suggested Simple Ratio.	Weight Percentage of A Required by Ratio.	Weight Percentage of A Found by Experiment.	Difference Weight Percentage.
A	B							
<i>o</i> -Phenylenediamine	<i>m</i> -Dinitrobenzene	1	39.99	1 : 1.50	2 : 3	30.01	30	0.01
<i>m</i> -Dinitrobenzene	<i>m</i> -Phenylenediamine	2	34.94	1 : 1.86	—	—	45.5	—
Benzamide	<i>m</i> -Nitrophenol	3	44.38	1 : 1.25	4 : 5	41.06	41	0.06
Benzamide	<i>p</i> -Nitroso-dimethylaniline	4	28.14	1 : 2.55	2 : 5	24.39	24	0.4
Picric Acid	Benzo-phenone	5	29.06	1 : 2.44	2 : 5	33.46	34	0.5
<i>m</i> -Dinitrobenzene	Naphthalene	6	40.2	1 : 1.49	2 : 3	46.66	46.87	0.2

of the liquidus curve of a eutectiferous system did not meet at a point ; in other words, to show that the solid eutectic mixture could not exist in contact with a liquid of variable composition. This group of experiments is therefore one of the few in which an examination of mixtures of approximately the eutectic composition was the primary purpose of the research.

^o H. M. Glass, W. M. Madgin and F. Hunter, *J. Chem. Soc.*, 1934, 260.

¹⁰ H. M. Glass and W. M. Madgin, *J. Chem. Soc.*, 1934, 1292.

Of the thirteen eutectic compositions considered in Tables II. and III., eleven fall at or near simple ratios. It is to be noted that in none of the original papers is the eutectic composition given nearer than half of one weight percentage. Also, because with one exception all their results are given in weight percentages, it is evident that the authors had not considered the possible existence of a rule. Therefore their determinations must be regarded as free from any subconscious bias.

The results given in Table II. must be accepted without discussion, because freezing-point data are not given and the curves therefore cannot be reconstructed. Puschin and Rikovski's curves, on the other hand, can be redrawn and some assessment made of their experimental accuracy. This has been done, and the results obtained for systems 3, 4 and 6 are in close agreement with those given in the original paper. For the other systems the conclusions are not so satisfactory. In each case it would appear that there had been a certain amount of super-cooling of one or both of the constituents and that the exact eutectic compositions are still uncertain. The fact that an exact ratio has been found in system 1 must therefore be somewhat discounted. On the other hand, if it be assumed that *m*-dinitrobenzene is a compound particularly prone to super-cooling and that neither of the phenylenediamines super-cool to an appreciable extent, then the value of 30 weight per cent. given in the original paper can be accepted for system 1 and in system 2 the eutectic would contain about 44 weight per cent. of *m*-dinitrobenzene. Thus a ratio here of 1 : 2 is not out of the question.

In the paper on metallic eutectics¹¹ it was shown that there were two ways of considering the ratios. It is as if there were two walls each built of bricks of two different colours. We can take a ratio between the numbers of bricks of different colours, as here the ratio between the numbers of constituent molecules has been considered, or we can take a ratio between the numbers of bricks in each wall, irrespective of the colour. The first kind of ratio has been named the constituent ratio, the second the phase ratio. In the latter case, allowance is made for solid solution and compound formation. In the case of metallic systems it has been shown that there cannot be exact simple ratio rules to embrace both types of ratios, but in the seven metallic systems considered the curious result was obtained that if one rule is exact the other is correct to 1 part in 200. Where the constituent ratios are somewhat complicated as 4 : 19 and 8 : 47 in the case of the copper-aluminium and copper-magnesium systems mentioned earlier, the phase ratios are often much simpler. These two systems, for example, give phase ratios of 1 : 1 and 7 : 9.

It might be that if data were available for obtaining the phase ratios for the systems considered in this paper, there would be further simplification and the four anomalous systems would fall into line. At present, as very little is known about solid solution formation in either salt or organic systems, very little can be done. It is known that an unstable compound, *m*-(C₆H₄(NO₂)₂)₂C₁₀H₈ is formed in the *m*-dinitrobenzene-naphthalene system. In this case, provided no solid solutions are formed, the phase ratio is 1 : 2 while the constituent ratio is 2 : 3. It is also known that, if one or two systems be excepted, solid solution formation in the nitrate systems given in Table I. is extremely limited, but a small solid solubility may have a large influence on the phase ratio. Thus

¹¹ Stockdale, *Proc. Roy. Soc., A*, 1935, 152, 96.

in the potassium nitrate-strontium nitrate system, if strontium nitrate can dissolve only 1.6 per cent. by weight of potassium nitrate at the temperature at which the eutectic mixture freezes, the phase ratio is 1 : 1.

The only one of these salt systems about which there is much information with regard to the solid solubilities is the potassium nitrate-ammonium nitrate system. Laybourn and Madgin find that ammonium nitrate will dissolve 8 per cent. by weight of potassium nitrate, and potassium nitrate 65 per cent. of ammonium nitrate;¹² that is to say, the molecular solubilities are respectively 6.44 and 70.1 per cent. The phase ratio is then 1 : 3.80, but if the eutectic were at 11.13 instead of 11.33 molecular percentages of potassium nitrate, this ratio would be exactly 1 : 4. A constituent ratio of 1 : 8 demands a eutectic containing 11.11 per cent. of potassium nitrate.

The evidence so far considered is indefinite, but it does at least suggest that simple ratio rules may exist. However, they cannot be proved or disproved until more exact experimental data are available. It is the purpose of this paper to bring forward this suggestion, in the hope that more experimental evidence may be forthcoming.

Summary.

The suggestion that in binary eutectic mixtures the ratio between the number of molecules of each constituent is simple has been examined. Calculations have been made for certain systems containing two salts with a common ion and for certain organic mixtures. The results obtained are not conclusive, but they do at least indicate that it may be possible to establish empirically a rule of simple ratios.

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¹² *J. Chem. Soc.*, 1933, 236.

THE PHOTO-SENSITISATION OF FILMS OF POTASSIUM BY MEANS OF HYDROGEN.

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Exposure of a potassium surface to molecular hydrogen has been shown by Suhrmann^{1, 2} to be insufficient to produce photo-electric sensitisation, and a discharge through hydrogen likewise has no effect unless the polarity of the surface is such that hydrogen ions can strike it, and then a large increase in the photo-emission is obtained. Surfaces prepared in this way have colours quite different from that of an ordinary surface and have been shown by an X-ray diffraction pattern obtained by Kluge and Rupp³ to consist of small crystals of potassium hydride as well as potassium. Lukirsky and Ryanoff indeed^{4, 5, 6} believe that the

¹ Suhrmann, *Physik. Z.*, 1928, **29**, 811.

² Suhrmann and Theissing, *Z. Physik*, 1928, **52**, 453.

³ Kluge and Rupp, *Physik. Z.*, 1931, **32**, 163.

⁴ Lukirsky and Ryanoff, *Z. Physik*, 1932, **75**, 849.

⁵ Lukirsky, *Physik. Z. Sowjet.*, 1933, **4**, 222.

⁶ Ryanoff, *Z. Physik*, 1931, **77**, 325.

surface responsible for the high emission consists of a monatomic layer of potassium adsorbed on potassium hydride—a KHK surface. Lukirsky and Ryanoff have prepared these highly sensitive surfaces by allowing monatomic hydrogen prepared by dissociating hydrogen on a tungsten filament to come in contact with a potassium surface.

It is known that a potassium surface does not appear to react with molecular hydrogen, but that a clean tungsten surface instantly adsorbs hydrogen^{7,8}. The lattice constant of a potassium surface⁹ is 5.25 Å., while that of a tungsten surface is 2.56 Å., and the equilibrium distance apart of the two hydrogens in H₂ is from measurements of the moment of inertia 0.76 Å.¹⁰ It appears therefore, that the fact that hydrogen will not spontaneously react with a potassium surface is connected with the fact that, to do so, the atomic components of the molecule would have to be dragged apart. Barrer¹¹ has found that for the adsorption of hydrogen on charcoal an activation energy of 13 to 15 kilocalories is required, and that as the surface concentration rises, the activation energy increases, tending finally to 30 kilocalories. Barrer has shown that his specimens of charcoal were heterogeneous, the lattice constant of the most perfect graphitised particles being 3.4 Å., and the amorphous material anything up to 4.5 Å. It is reasonable to infer, therefore, that the lower activation energies are associated with adsorption on the perfect crystals and that, when these points are saturated, still further work must be done to drag the two hydrogen atoms in the molecule far enough apart to permit them to react with the distorted amorphous lattice. It was hoped therefore, that a measure might be obtained of the energy required to make molecular hydrogen react with a potassium surface. Unfortunately this energy proved so high that even heating the potassium film to 600° K. for five minutes in the presence of hydrogen at 10⁻² mm. produced little or no change in its photo-electric properties, and at any higher temperature changes began to occur due to evaporation or migration of the potassium. No measure of the activation energy of the required process has therefore been obtained and the results of this work give only figures for the thresholds of the various films studied.

Experimental.

The apparatus used consisted of two parallel tungsten filaments, one of ribbon 2 mm. wide and the other of wire 0.1 mm. thick. Around the filaments is a grid for collecting the photo-electrons and behind them a Kunsman source consisting of a filament coated with a mixture of Fe₂O₃, Al₂O₃, and K₂O^{12, 13} to provide the potassium films.

A Quartz monochromator with a pointolite source was used to provide the monochromatic light. A compensated valve bridge (Compton and Haring¹⁴ modified for use with the triode electrometer valve Osram type T) was used to measure the photocurrents. The circuit was placed in an earthed steel box in order that it should be shielded from both electrostatic and electromagnetic disturbances. The lead from the grid to the photocell was similarly shielded, and the cell itself protected as much as possible from extraneous light by blackened metallic tubing.

The photo-currents at different settings of the monochromator were

⁷ Roberts, *Camb. Phil. Soc.*, 1934, **30**, 74.

⁸ Roberts and Whipp, *Camb. Phil. Soc.*, 1934, **30**, 376.

⁹ Eucher, *Z. Physik*, 1927, **44**, 392.

¹⁰ Simon and Vohsen, *Z. physik. Chem.*, 1928, **133**, 165.

¹¹ Barrer and Rideal, *Proc. Roy. Soc. A*, 1935, **149**, 231.

¹² Compton and Haring, *Trans. Electro-Chem. Soc.*, 1932, **82**, 245.

obtained in the first instance by a deflection method, setting the galvanometer in the circuit to zero with the strip unilluminated. As the characteristic of the type T valve is curved over the working range this method is not strictly accurate, although the error involved in assuming linearity in the response will not be appreciable (above the limit of experimental variation) unless the photo-currents are large enough to produce a change in the anode current of the order of 100 micro-amps. In cases where this condition did not hold a compensating potentiometer circuit was set up and the photo-current to the grid balanced out against the current produced by applying a known potential from a potentiometer across a constant high resistance of 10^{12} ohms, prepared by filling a capillary tube with a solution of amyl alcohol in xylene.

For theoretical purposes it is necessary to know not only the emission, but also the emission per unit of radiant energy absorbed by the surface. The relative amounts of light absorbed at different wave-lengths could be most readily determined if the photo-sensitive strip filament could be used as a bolometer filament. This has been attempted and Table I. has been obtained measuring the amount of light absorbed from out of the balance current of the bolometer bridge.

These figures indicate that the amount of light absorbed is approximately uniform over the above range of wave-lengths so that it is permissible to use the readings from the valve bridge as a measure of the photo-emission per unit of absorbed light.

TABLE I.

Wave-Length. (Å.)	Relative Amount of Light Absorbed.
10,000	1.1
8,000	1.2
7,000	0.8
6,000	1.0
5,000	0.8
4,000	0.8

The Method of Finding Thresholds.

The old direct method consisted in plotting the emission against either the wave-length or frequency and finding the point at which the curve cuts the axis. The results obtained however depended on the accuracy with which the current could be measured; and as shown by Fowler¹³ the intercept of the curve with the axis is only strictly definite and a measure of the threshold at absolute zero of temperature; and at all higher temperatures it is possible to get some emission at frequencies below the threshold. Fowler has developed a method of obtaining the threshold from experimental observations at frequencies near the threshold. The method as usually employed by experimentalists is summarised by the equation:

$$\log (I/T^3) = B + F(x) \quad (1)$$

Where, I is the emission per unit of absorbed radiation; B a constant depending on the units chosen; T the temperature; F a universal function, the so-called Fowler function; $x = h(\nu - \nu_0)/kT$; ν the frequency of the radiation; ν_0 the threshold frequency; h Planck's constant; k Boltzmann's constant.

Equation (1) indicates that if $\log (I/T^3)$ be plotted against $h\nu/kT$, the curve obtained should be of a standard shape and when it moves horizontally by an amount $h\nu_0/kT$ and vertically by an amount B , should fit the theoretical curve of $\log I/T^3 = F(x)$.

Fowler's method which has been tested and shown to be accurate for clean surfaces by several experimentalists^{14, 15, 16} consists in finding the

¹³ Fowler, *Physical Rev.*, 1931, **38**, 45.

¹⁴ Dubridge and Roehr, *ibid.*, **B**, 1932, **39**, 99.

¹⁵ Dubridge, *ibid.*, 1932, **39**, 108.

¹⁶ Cardwell, *ibid.*, 1930, **36**, 203, 2041.

vertical shift required to make the experimental curve fit the standard curve. In practice this amounts to finding points on the experimental curve with the same slope as standard points on the theoretical curve. In short, we eliminate the constant B by a differentiation which is none the less real because it is implicit, rather than explicit; and if one were to carry out this differentiation before application of the theoretical relations, one should have a tidier and no less accurate method of arriving at ν_0 .

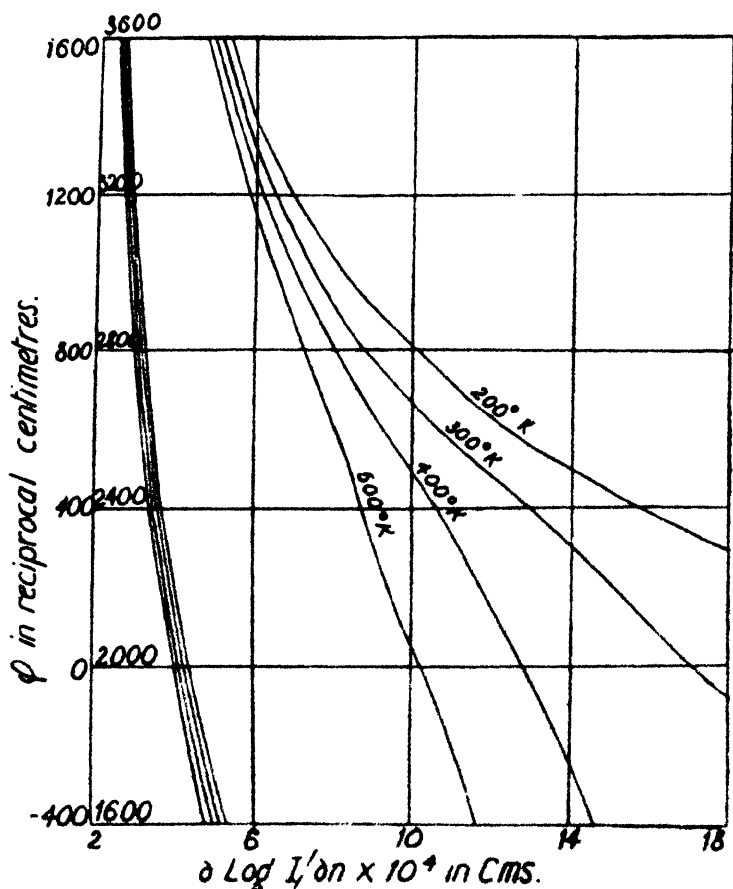


FIG. 1.—The function ϕ at four different temperatures. The figures on the right of the ordinate refer to the L.H.S. branch of the curves.

Differentiating equation (1), we have,

$$\begin{aligned} d \log (I/T^2)/dx &= F'(x), \\ \text{or } \frac{hT}{h} d \log (I/T^2)/d\nu &= F'(x). \end{aligned}$$

Where F' is the first derivative of the Fowler function. In practice one deals with the wave number,

$$n = \nu/c \text{ rather than the frequency } \nu \text{ or,}$$

$$\frac{hT}{hc} \left\{ d \log (I/T^2)/dn \right\} = F' \left\{ \frac{hc}{kT} (n - n_0) \right\}.$$

Inserting numerical values and interposing,

$$n - n_0 = \frac{T}{1.432} \mathcal{E}_1 \left\{ \frac{T}{1.432} d \log (I/T^2) / dn \right\} \quad (2)$$

$$= \phi(T, d \log (I/T^2) / dn). \quad (3)$$

Where \mathcal{E}_1 is used for the inverse function of F' . Equation (3) expresses the fact that under the circumstances in which Equation (1) holds, viz. ; for n not far from n_0 , $n - n_0$ is a universal function of T and $d \log (I/T^2) / dn$ no matter in what units I may be measured. Equation (2) shows how ϕ is to be calculated.

If the measurements are carried out at one temperature (as in practice they usually are) ; equation (3) becomes

$$n - n_0 = \phi(T, d \log I / dn) \quad (4)$$

and, further ϕ proves to be a relatively slowly varying function with respect to T , so that, if the values of ϕ are calculated at $T = 300^\circ \text{K.}$, the tables obtained may be used on all experimental results obtained at ordinary laboratory temperatures ($300 \pm 5^\circ \text{K.}$). In Fig. 1 curves are given showing $d \log I / dn$ plotted against ϕ at various temperatures ; 200°K. , 300°K. , 400°K. , and 500°K. For clearness the curves have been split into two sections and in the branch on the left the axis of ϕ has been shifted 2,000 reciprocal centimetres vertically downwards.

The curves show that for all values of n greater than n_0 the values of ϕ may indeed be taken as independent of T . The variation of ϕ at $d \log I / dn = 5$ for example being only 240 cms. for a change in temperature of 300°K. Such a variation would only mean an error of 60 Å. at 5000 Å.

Accordingly all that is needed to use the above curves in measuring thresholds is to measure I at two different frequencies, obtain $d \log I / dn$ and, knowing the temperature to within a few degrees, read off ϕ from the appropriate curve. This ϕ is equal to the mean distance of the threshold from the two points at which I was obtained.

Table II. (which expresses the results of measurements on a film of potassium on tungsten) shows how the method is to be applied. Columns (1) and (2) give the wave-length λ , and the experimental measurements of I , columns (3) and (4) $\log I$ and n , column (5) $d \log I / dn$ obtained by drawing tangents to the plot of $\log I$ versus n , column (6) the corresponding values of ϕ read off from the theoretical curves and column (7) n_0 equal to

TABLE II.

λ .	I .	$\log I$.	n .	$d \log I / dn$.	ϕ .	n_0 .
5500	120	2.08	18,180	1.7	5000	13,180
6000	66.0	1.82	19,670	3.0	2900	13,770
6500	22.5	1.35	15,380	6.5	1280	14,100
6800	4.6	0.66	14,710	0.4	740	13,970
7000	1.5	0.18	14,290	10.8	600	13,690
7200	0.4	1.00	13,890	18.2	- 140	14 030

$n - \phi$. The last column shows very satisfactory consistency for all points except the first, the one furthest removed from the threshold. This consistency confirms both the accuracy of the above method and also the applicability of the Fowler relation to composite films, a point which incidentally has previously been tested and confirmed by Brady¹¹ in the case of potassium films on silver.

¹¹ Brady, *Physic. Rev.* 1834. 46, 9, 768.

Results.

It has been possible to produce a film of standard properties in the following way. The filament was first flashed at 2500°K. , cooled and a thick deposit given to it by the Kunsman source. The bulb attached to the photo-cell was then immersed in liquid air and excess potassium over and above the equilibrium film allowed to distil off on to the cooled glass.

TABLE III.

λ in Å.	I
4000	5.8
4500	13.0
5000	14.0
5500	12.7
6000	5.3
6200	3.3
6500	1.7
6800	0.4

TABLE IV.

Relative Number of Hydrogen Atoms Incident of the Surface.	λ° .
0	7200
20	6900
24	6600
40	6400
60	6100
80	5800
120	5700

After about one hour the film attained constant photo-electric properties and no further change could be observed even in 24 hours. Table III. gives the properties of this film.

The film therefore has a flat selective maximum emission at 5000 Å. and a threshold measured by the method given above of 7140 Å., a figure which when compared with the 5700 Å. found by Ives and Olpin¹⁸ for bulk potassium shows that the film must be a thin one and probably the monatomic layer WK.

TABLE V.

λ	I
4000	2.6
4500	4.1
5000	4.9
5500	5.4
6000	6.6
6500	7.1
7000	5.8
7500	2.3
7800	0.95
8000	0.46
8100	0.25

From which
 $\lambda_0 = 8300 \text{ Å.}$

TABLE VI.

λ	I
4000	12.1
4500	19.6
5000	14.0
5500	10.4
6000	9.6
6500	8.5
7000	7.3
7500	5.0
8000	2.8
8500	0.35

From which
 $\lambda^{\circ} = 9200 \text{ Å.}$

If now this film be exposed to molecular hydrogen at a pressure of 10^{-4} mm. for periods of the order of an hour or even heated to 600°K. in this gas no change whatever is produced in the emission obtained on pumping out the gas. But if the wire filament is heated in the presence of hydrogen to 1500°K. and a beam of atomic hydrogen thus fired on the strip filament, the photo-emission at all wave-lengths decreases and the threshold moves towards the ultra-violet. The

actual number of hydrogen atoms striking the surface would not be easy to compute, but the relative number may simply be obtained as the product of the pressure and the time of heating the wire filament; Table IV. indicates the progress of the threshold shift as the film is treated with atomic hydrogen.

If now over the inactive film thus produced fresh potassium is deposited and allowed to come into equilibrium with bulk potassium at liquid air temperature a highly sensitive film is produced, as Table V. indicates.

¹⁸ Ives and Olpin, *Physic. Rev.*, 1929, 34, 117.

This sensitive film if treated with hydrogen will in a similar way gradually lose its emission but regain it on treatment with potassium vapour. The sensitive film above is probably a WKHK film, the insensitive one from which it was derived the WKH film. There is a way of getting films with still higher thresholds, that is by treating the filament immediately after flashing with hydrogen and then depositing the potassium over the resultant WH surface. Table VI. gives the emission.

This is probably the WHK film. It has been proved by Roberts (*loc. cit.*) that hydrogen is strongly adsorbed by tungsten and the WH surface is far more electronegative than the tungsten surface; and so, it is to be expected that any positive film adsorbed on this surface would be more strongly polarised than on tungsten. The WHK films are therefore expected to exhibit the same high sensitivity as the WOCs films studied by Kingdon¹⁰, and as the table above illustrates they do.

Collecting then the experimental results we have for the thresholds of the various surfaces studied the following figures :—

WK	7140 Å.	= 1.72	Electron Volts
WKH	5700 Å.	= 2.16	" "
WKHK	8300 Å.	= 1.49	" "
WHK	9200 Å.	= 1.34	" "

Summary.

Monatomic films of potassium on tungsten have been prepared and examined photo-electrically. These films will not react with molecular hydrogen at room temperature or at any temperature below the volatilising point. The films do, however, react with atomic hydrogen to form a WHK surface which is capable of absorbing fresh potassium to give a sensitive WKHK surface. A still more sensitive surface may be prepared by depositing potassium on a WH surface.

A graphical method of obtaining the threshold from two readings of photo-emission of different frequencies near the threshold, is derived from Fowler's equation for photo-electric emission.

The author desires to express his gratitude to Professor E. K. Rideal for his interest in this work and for many helpful suggestions, to the Royal Commissioners for an Exhibition of 1851 and to Trinity College, Cambridge for a grant.

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¹⁰ Kingdon, *Physic. Rev.*, 1924, **24**, 510.

¹¹ Kunsman, *Science*, 1925, **62**, 269.

¹² Kunsman, *J. Franklin Inst.*, 1927, **203**, 635.

THE KINETICS AND HEAT OF ADSORPTION OF ETHYLENE BY PLATINUM.

BY E. B. MAXTED AND C. H. MOON.

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The adsorption of ethylene by catalytically active metals is of considerable importance in connection with the kinetics of hydrogenation reactions. Adsorption by metals other than platinum (*vis.* nickel, copper and iron) has already been studied by several workers,¹ principally

¹ Griffin, *J. Amer. Chem. Soc.*, 1927, **49**, 2136; Foresti, *Gazz.*, 1929, **59**, 243; Magnus and Klar, *Z. physikal. Chem.*, A, 1932, **161**, 241.

from the standpoint of the variation of the amount adsorbed with the pressure. In general, the ethylene isotherms, unlike those of hydrogen, were found to be of the continuous type; and the adsorption was, under equivalent conditions, less than that of hydrogen. For platinum, figures giving the total adsorptive power at atmospheric pressure are available,³ on the basis of which ethylene may apparently be adsorbed to a slightly greater extent than hydrogen; but, in any case, few published data exist on the progress of the adsorption with time, and it has therefore been considered of interest in the present work to study the kinetics of the adsorption process.

In addition, measurements have been made of the heat of adsorption of ethylene on platinum. This subject has recently assumed importance in connection with the possible contribution⁴ of the adsorption heat towards the activation energy of a hydrogenation reaction in its catalysed form.

It was found essential, in order to obtain consistent results, both for the kinetics and for the heat of adsorption, to take great care to free the platinum from adsorbed gases other than ethylene; and it should be emphasised that measurements carried out with platinum black which has not been previously brought into this condition possess little significance. In its freshly prepared state, platinum black contains oxygen, which may be removed by repeated treatment with pure hydrogen, in the first instance at room temperature and subsequently at 100°, each treatment being followed by prolonged degassing to remove the water formed. In the first of these treatments, hydrogen was admitted in small increments to avoid the danger of sintering. The subsequent complete elimination of the residual adsorbed hydrogen and its replacement by ethylene involves a large number of treatments with the latter gas, each treatment being followed, as before, by degassing. The progress of the replacement is most conveniently followed by observing the apparent value for the heat of adsorption of ethylene, which gradually sinks from a relatively high value—in which heat of reaction of the ethylene with residual adsorbed hydrogen is included in the apparent heat of adsorption—to a constant lower value corresponding with ethylene adsorption only.

Experimental.

The apparatus employed is shown diagrammatically in Fig. 1. The platinum black, prepared by Mond, Ramsay and Shields' method,⁴ which weighed 16.57 g., was contained in the calorimeter bulb, A, which, together with the first few centimetres of its connecting tube, was constructed of Pyrex glass blown as thin as possible in order to reduce its heat capacity to a minimum. We produced a bulb and connecting tube which, with a capacity of about 5 c.c., only weighed about 0.3 g. This was fused to tubing of normal wall thickness at the point shown, and was surrounded by a second bulb, B, which could be evacuated to form a small Dewar vessel, or filled with gas when a conducting enclosure was required in order to bring the platinum to the temperature of the surrounding bath. The rise in temperature during heat measurements was recorded on a rotating drum by a Moll reflecting galvanometer connected with the thermo-element, C. After trial, it was found preferable to insert this thermo-element in a

³ See, for instance, Taylor and Burns, *J. Amer. Chem. Soc.*, 1921, 43, 1273.

⁴ Zur Strassen, *Z. physikal. Chem.*, A, 1934, 169, 81; Schwab, *ibid.*, 171, 421; Maxted and Moon, *J. Chem. Soc.*, 1935, 1190.

⁴ Mond, Ramsay and Shields, *Phil. Trans.*, A, 1895, 186, 657.

Pyrex sheath tube in such a way that it was surrounded by gas at constant pressure, the sheath being drawn out to the thinnest possible wall in the neighbourhood of the thermo-junction. By this means, the influence on the galvanometer deflection of the necessarily large change in the gas pressure—and in the conductivity of the gas surrounding the thermocouple, if this is not isolated—which occurs on and after admitting gas to the degassed metal, was avoided.

A normal vacuum calorimeter method cannot readily be used with ethylene on account of the smallness of its adsorption at low pressures; for this reason, the integral heat at constant, atmospheric pressure was measured in place of admitting small increments at a low, and continuously varying, pressure, it having previously been found that in many cases the

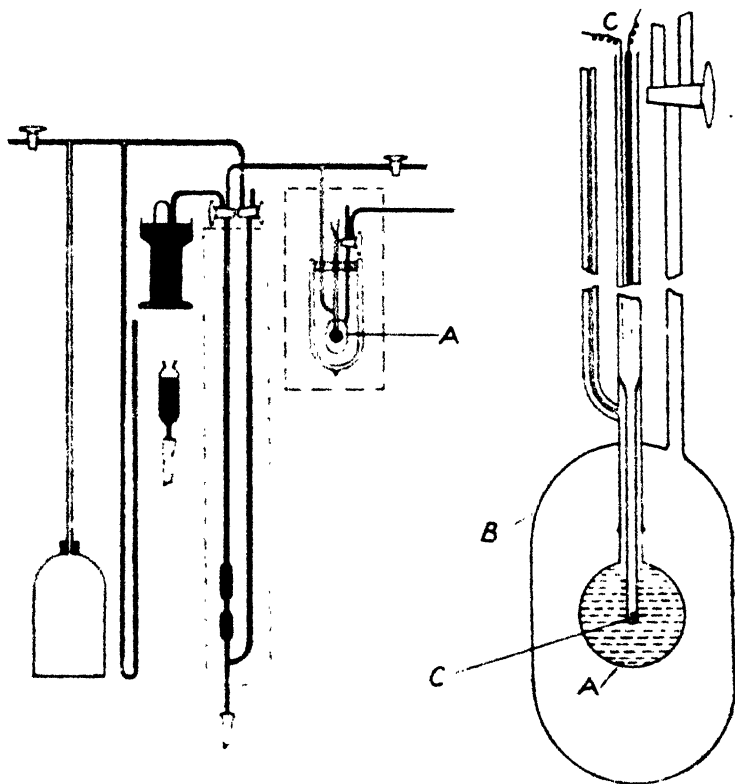


FIG. 1.

differential heat is independent of the amount adsorbed^a and is thus identical with the adsorption heat measured when, as in the present case, a larger increment is added in one stage. The maintenance of a constant gas pressure within the calorimeter during the adsorption also renders more constant the rate of distribution of heat, by conduction, throughout the mass of adsorbent—which consists of metallic particles in incomplete contact with one another and, for the greater part, separated by gas—and simplifies the form of the heat loss factor in the observed heating curve, by the extrapolation of which the true rise in temperature is calculated.

This atmospheric pressure method was tested with hydrogen diluted

^a Ward, *Proc. Roy. Soc., A*, 1931, 133, 506; Beebe, *Trans. Faraday Soc.*, 1932, 28, 761; Maxted and Hassid, *J. Chem. Soc.*, 1931, 3313; *Trans. Faraday Soc.*, 1933, 29, 688.

with helium or argon, and was found to give heat values consistent with those given for hydrogen on platinum by the vacuum calorimeter method. Moreover, the adsorption heat was, in conformity with previous observations, independent of the volume of hydrogen adsorbed, which could be varied by varying the degree of dilution of hydrogen with the inert gas.

All gases were carefully purified before use; ethylene by liquefaction and fractional distillation; hydrogen by desorption from palladium; and traces of oxygen were eliminated from inert gases by admixture of a small proportion of hydrogen, followed by repeated treatment with heated platinum. In some cases, the inert gases were previously subjected to prolonged sparking with oxygen in order to remove possible traces of nitrogen, followed by the removal of the excess of oxygen by flashing with phosphorus. Such sparked specimens of argon or helium gave, however, identical results with untreated specimens, since both of these gases were already in a high state of purity and, in any case, traces of nitrogen do not contribute to the observed heat effect, whereas even a small degree of contamination with oxygen leads to too high apparent heat values. The gases other than ethylene were of course only used for testing the method of heat measurement employed. Save for a preliminary stabilising period at 200°, the platinum was not subjected to a higher temperature than 100°, and all degassing was carried out at this temperature by means of a combined Hyvac and mercury vapour pump.

Kinetics of the Adsorption.

The progress of adsorption of ethylene with time, in a typical measurement at 20°, is given in Table I. If the figures are plotted graphically, it will be seen that the course is of normal type, namely that a large part of the adsorption takes place almost instantaneously, this relatively rapid primary adsorption being followed by a much slower secondary process. This secondary adsorption follows Ward's⁶ relationship, in which the ratio of the adsorption to the square root of the time is a constant, and, consequently, also Bangham and Burt's equation,⁷ which involves a linear relationship between $\log v$ and $\log t$. These simple linear variations do not, of course, hold for the total adsorption, which includes the distinct primary process; and their inapplicability to the total process, together with their validity for the secondary adsorption, may be regarded as additional evidence for the presence of the two distinct adsorption components. The agreement with Ward's relationship is shown in Table II., in which v is the additional adsorption after the first two minutes.

TABLE I.

Time.	C.c. at N.T.P. of Ethylene Per Gram Pt.
20 secs.	0.346
40 "	0.366
1 min.	0.376
2 "	0.385
5 "	0.40
10 "	0.41
30 "	0.43
1 hr.	0.45
3 "	0.50
7 "	0.56
10 hrs. 47 mins.	0.59
22 "	0.70

TABLE II.

t , in Mins.	v , in c.c. at N.T.P. per g Pt.	v/\sqrt{t}
3	0.015	0.0087
8	0.025	0.0088
28	0.045	0.0085
58	0.065	0.0085
178	0.115	0.0086
418	0.175	0.0086
645	0.205	0.0081
1318	0.315	0.0086

⁶ Ward, *Proc. Roy. Soc., A*, 1931, **133**, 522.

⁷ Bangham and Burt, *Proc. Roy. Soc., A*, 1924, **108**, 481.

The influence of pressure on the amount adsorbed was also investigated, the isotherm being of the continuous type, as in the adsorption of ethylene on other metals. This is shown graphically in Fig. 2, which refers to the

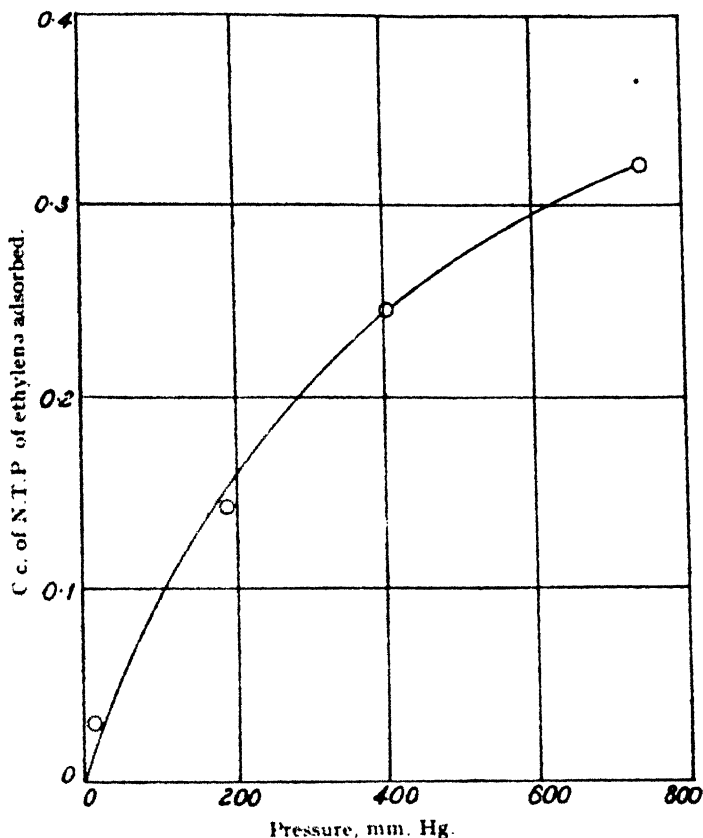


FIG. 2.

adsorption by 16.57 g. Pt at room temperature, after one minute, at which time the primary adsorption is substantially complete and the secondary adsorption still small.

Heat of Adsorption.

The following preliminary measurements were made with hydrogen, in order to test the method. The volume of hydrogen present in the calorimeter bulb on admission of gas to the previously degassed platinum was reduced to any desired low value by diluting the gas with argon or helium; and, in every case, the whole of the hydrogen in the bulb was completely and rapidly adsorbed by the relatively large mass of platinum employed. The rapid progress and subsequent cessation of the adsorption at a value corresponding with the available hydrogen could be followed by the gas burettes. The calorimeter* was surrounded by a constant temperature

* The use of a large insulated enclosing box, for all parts of the apparatus in the neighbourhood, maintained at a constant temperature by means of a small fan with appropriate heating and cooling coils (a necessary provision, in view of the so-called "gas effect," in the case of adsorption heat measurements with a vacuum calorimeter) was found not to be essential, since the results obtained with this larger enclosure were identical with those given when only the vacuum vessel containing the calorimeter was thus shielded.

enclosure. In the measurements summarised in Table III., those of Series (a) were preceded by a degassing period of 12 hours at 100°, and those of Series (b) by a similar period at room temperature. All determinations were carried out at 18°. The gas mixtures employed were made up approximately only of the composition given, since the exact adsorption was read off directly.

The observed adsorption heat thus varies about a mean value of about 18 k. Cals. in Series (a) and 17 k. Cals. in Series (b); the limits of accuracy of the method (measured by the deviation, in individual determinations, from this mean) is approximately of the same order as for the vacuum calorimeter previously used.* There was, as before, no indication of a definite decrease or increase of the adsorption heat with an increase in the adsorbed concentration. The value previously found by the vacuum calorimeter method for the adsorption of hydrogen on platinum black in approximately the same condition was about 17 k. Cals. or, in some cases, less; and, in view of the experimental difficulties which attend the direct measurement of adsorption heats, including the possible variation in the heat value with the state of the platinum, a greater degree of reproducibility is not probable. It may be noted, further, that, in all cases, the rapid adsorption of only a small volume of gas by a relatively large mass of platinum is involved: accordingly, the heat measured is principally, if not exclusively, that of the primary adsorption.

TABLE III.

Percentage of Hydrogen in Mixture.	Nature of Inert Gas.	Vol. in c.c. at N.T.P. of Hydrogen Adsorbed.	Q, in k. Cals. per g. Mol. Hydrogen.
<i>Series a.</i>			
13.4	Helium	0.39	18.0
13.4	Helium	0.61	17.6
17	Argon	0.97	18.5
15	Argon	0.91	17.4
15	Argon	0.90	17.4
12	Argon	0.74	18.5
7.5	Argon	0.45	19.1
<i>Series b.</i>			
15	Argon	0.69	17.1
12	Argon	0.56	17.2
7.5	Argon	0.36	16.5

TABLE IV.

Run No.	Vol. in c.c. at N.T.P. of Ethylene Adsorbed.	Q, in k. Cals. Per g. Mol. of Ethylene Adsorbed.
1	0.54	9.0
2	0.55	9.1
3	0.48	8.6
4	0.41	9.5
5	0.42	8.9
6	0.35	7.8
7	0.37	8.8
8	0.39	9.1
9	0.40	7.7
10	0.41	9.6
11	0.58	9.6

Measurements were now carried out with ethylene, for which the vacuum calorimeter is inapplicable. The presence of residual adsorbed hydrogen leads, as already stated, to too high apparent heats of adsorption; and the value of Q gradually fell from slightly over 30 k. Cals. to a constant value of about 9 k. Cals. as the residual hydrogen was removed. The higher apparent values include heat of reaction in addition to heat of adsorption. The approximate constancy of the adsorption heat after this preliminary stage of hydrogen removal has been passed is shown in Table IV. Pure ethylene, undiluted with an inert gas, was used throughout. A few comparative tests, not included in the table, were, however, made with ethylene-helium mixtures—in which case the adsorption of ethylene was, of course, considerably smaller—and were found to give similar heat values.

The heat effect observed in measurements Nos. 6 and 9 of the above series is considerably below the average (about 9 k. Cals.), but has been

* *J. Chem. Soc.*, 1931, 3313.

included for completeness of record. The platinum was in every case previously degassed for 12 hours at 100°, save before measurement No. 11, for which the degassing temperature was 200°. Over 95 per cent. of the total adsorption observed during the period of each heat measurement (5 minutes) occurred in the first 2 minutes. All determinations were at 18°.

Summary.

The secondary adsorption of ethylene by platinum black, namely the slow process which takes place subsequently to the almost immediate primary adsorption, follows the relationship previously observed by Ward for hydrogen on copper, according to which the ratio of the volume adsorbed to the square root of the time is a constant. It consequently also agrees with Bangham and Burt's general equation, which involves a linear relationship between $\log v$ and $\log t$.

Since the normal vacuum calorimetric method is inapplicable to ethylene, on account of its small adsorption at low pressures, a calorimetric method involving adsorption at atmospheric pressure has been developed for the measurement of the adsorption heat. This was tested for hydrogen diluted with an inert gas, and was found to give an adsorption heat of approximately the same value as that previously determined in the normal way. On applying the method to ethylene, a molecular heat of adsorption of about 9 k. Cals. was observed. It is necessary in all cases, both for the measurement of the kinetics and of the heat of adsorption, to subject the platinum to preliminary treatment to remove residual adsorbed gases other than ethylene.

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THE COLLISION MECHANISM AND THE PRIMARY PHOTOCHEMICAL PROCESS IN SOLUTIONS.

By E. RABINOWITCH AND W. C. WOOD.

Received 28th May, 1936.

(1) The Collision Number and the Collision Intervals.

The mean *number of collisions*, z (gas), of a gas molecule under NTP conditions is of the order of 10^{10} per second. The average *duration of a collision*, τ ,—i.e. the time during which the interaction energy is not small compared to kT —is about 10^{-13} to 10^{-12} secs. The order of magnitude of τ is the same for collisions of saturated molecules and those of free atoms or radicals. Only collisions of complicated particles possessing many degrees of freedom and low frequencies corresponding to the interchange of energy between them, can last for longer than 10^{-12} secs.

The average *collision interval* θ (gas) (because of the smallness of τ) is practically equal to $1/z$ (gas).

We now consider collisions between the molecules of a *solute* (not their collisions with the molecules of the solvent), and compare them with the collisions of the same molecules in the gaseous state. In the case of a strong interaction between solute and solvent, leading to the formation of solvates or of clusters of solvent molecules surrounding the dissolved particles, all the three quantities z , τ and θ may be affected by dissolution.

In the case of a weak interaction, as presented for instance by solutions of permanent gases, or of iodine in carbon tetrachloride, the average values of z , τ and θ may remain practically unchanged. The collision duration τ , in particular, must remain unaffected by the presence of the solvent, if the interaction of the colliding particles and their kinetic energy are independent of the solvent. If, in addition, the solvation energy of a colliding pair (Fig. 1a), is not different from that of the two separated particles (Fig. 1b), then the probability of finding two given molecules in the state of collision must be the same in the gaseous and in the dissolved state. The aggregate time spent by a molecule in the collision-state during a second will therefore be the same in both cases. This total collision-time is equal to $z\tau$. With $(z\tau) (\text{sol}) = (z\tau) (\text{gas})$ and $\tau (\text{sol}) = \tau (\text{gas})$, the collision number $z (\text{sol})$ must be equal to $z (\text{gas})$ as well.

The purpose of this paper is to show that even in this ideal case of a solution which leaves the average values of z and θ unchanged, the *distribution* of collisions is changed in a significant manner. In a gas, the actual values of the collision-intervals are distributed according to the usual statistical law, the probability of an interval θ being proportional to $e^{-\theta}$. In a closely-packed medium, *the collisions occur in sets*. The

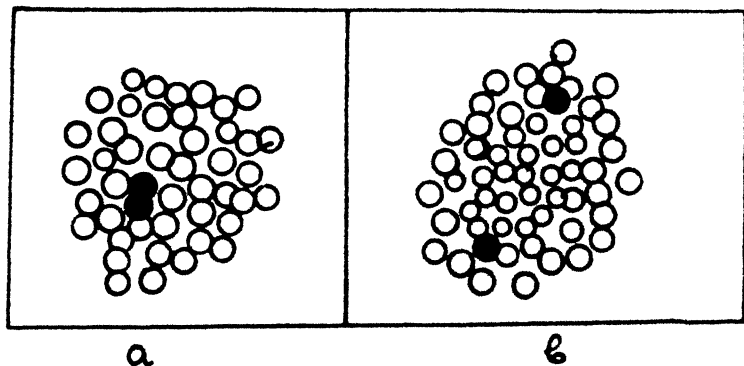


FIG. 1.

intervals θ between the collisions belonging to one set are very short, while those Θ between the sets are correspondingly longer. If the average number of collisions in a set is \bar{n} , then the average length of the inter-set intervals must be $\Theta = \bar{n}\theta_{(\text{gas})}$, in order that the total collision number z may remain unchanged.

The occurrence of collision-sets is due to the fact that the colliding pair of particles is surrounded by the molecules of the solvent and can escape from this "cage" only by a process of diffusion during which it has an opportunity of colliding several times.

To illustrate this consequence of a high concentration of the molecules in a solution, we constructed a simple model, shown schematically in Fig. 2. It consists of a flat brass plate (1) with a zig-zag border (2), and an insulated knob (3) in the centre. The knob is connected to one pole of the battery, the plate itself to the other pole. A number (20-60) of small balls are distributed on the plate. All but one of them are insulated, and represent the molecules of the solvent. The one non-insulated ball and the central knob represent two dissolved molecules; every time they come into contact (as shown in the figure) a circuit is closed and the collision registered by a lamp or by an electro-magnetic recording mechanism on a drum.

The plate is placed on a shaking machine and the balls brought into strong agitation. The zig-zag border aids in transforming the regular movement of the machine into a chaotic agitation of the balls. Fig. 3 shows two sections of the recording; Fig. 3a was made with 25 balls on the plate; Fig. 3b with 50 balls. The "intermittent" character of the collision mechanism at high densities is clearly shown by this figure. Table I. gives the results of registering the collisions for about 10 mins. at different densities. Column (1) shows the number of the insulated balls; column (2) the proportion of the surface covered by the balls; column (5) the average number of collisions per second. Column (4), which contains the average number of collisions per set, is illustrated by Fig. 4. A comparison of columns (4) and (5) shows that *whereas the total number of collisions (z) remains practically unchanged, the average length of the series (\bar{n}) increases very sharply after a certain density has been exceeded.*

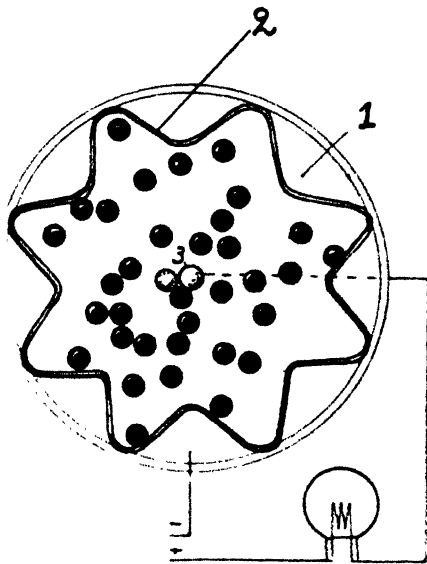


FIG. 2.

The addition of one ball to 51 causes the trebling of \bar{n} , without producing any change in z .

It is, of course, only with the greatest caution that the quantitative results obtained with this two-dimensional macroscopic model may be

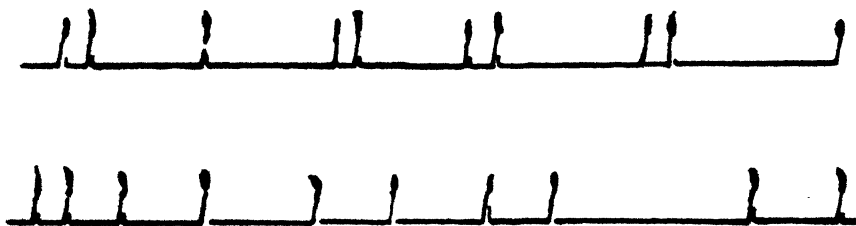


FIG. 3a.



FIG. 3b.

used for real three-dimensional molecular systems. It is, however, safe to assume that in these systems also, the average length of the collision-sets increases very sharply at higher densities. The essential question is: to what section of the curve in Fig. 4 does the real liquid correspond?

TABLE I.

N.	σ .	Number of Series with \bar{n} =										\bar{A} .	\bar{z} .
		1.	2.	3.	4.	5.	6.	7.	8.	9.	10 and more.		
25	0.36	263	22	4	4	—	—	—	—	—	—	1.15	0.52
35	0.49	149	67	37	17	4	2	1	—	—	—	1.8	0.57
48	0.66	40	41	32	16	16	12	5	3	4	4	3.3	0.56
50	0.69	11	10	8	12	7	4	8	10	3	12	6.3	0.52
51	0.70	11	6	12	4	2	5	4	3	6	26	7.4	0.56
52	0.715	5	5	—	3	—	3	1	—	—	17	20.4	0.57
(1)	(2)	(3)										(4)	(5)

If we consider, for instance, liquid argon with a molecular weight about 40 and a density 1.4, we find that 1 c.c. contains about 1.9×10^{23} molecules. The volume of an argon molecule is about 1.3×10^{-23} c.c.; the total volume of the molecules contained in 1 c.c. of the liquid is thus

0.25 c.c. In the case of CCl_4 , to take another example, 6×10^{21} molecules are contained in 1 c.c. of the liquid, with an aggregate volume of about 0.35 c.c. A volume density of 35 per cent. occupied space corresponds to a two-dimensional density of about 50 per cent. occupied surface. This density produces, according to our experiments, collision-sets with an average length of about 2. This estimate of the average length of collision-sets in real solutions is confirmed by considerations of the diffusion coefficients. According to Einstein and Smoluchowski the mean displacement Δ of

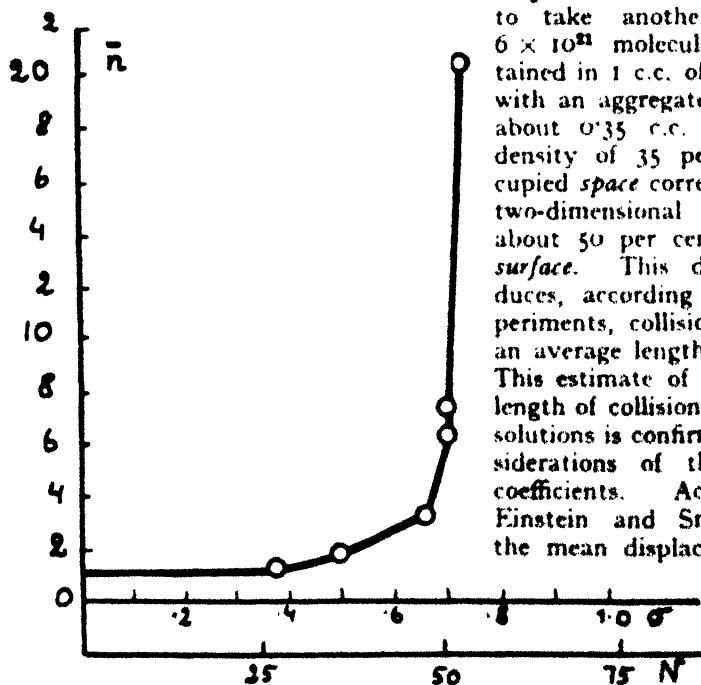


FIG. 4.

coefficient D by the equation

$$\bar{\Delta}^2 = 2Dt \quad (1)$$

In a liquid, even a displacement over a distance equal to a single molecular diameter (say $\Delta = 3 \times 10^{-8}$ cm.) is achieved on a complicated zig-zag path consisting of a great number of single segments. The statistical

equation (1) can therefore be applied even to such small displacements. The diffusion coefficients of uncharged molecules in solutions of low viscosity (e.g. of iodine in carbon tetrachloride) are of the order of 2×10^{-5} . Inserting this value of D into (1) and assuming $\Delta = 3 \times 10^{-8}$ we obtain :—

$$t = 2.5 \times 10^{-11} \text{ secs.}$$

During this interval, the collision partners are agitating to and fro in a narrow space, without separating themselves so far as to allow a molecule of the solvent to slip between them. A gas molecule travelling at a speed 10^4 cm./sec. would cover a similar path, 3×10^{-8} cm., in 3×10^{-12} secs. The above calculated "separation interval," 2.5×10^{-11} secs. is ten times longer and will allow the particles to collide more than once, but probably not more than four or five times.

We may thus assume that collision-sets actually occur in solutions, but are on the average rather short, consisting of 1, 2 or 3 collisions. As confirmed by Table I., the probability of a collision-set consisting of n collisions is proportional to e^{-an} , where a is a constant depending on the density; single collisions are therefore the most frequent at all densities. Longer sets may occur in systems with higher density: highly viscous liquids, glasses or true solid phases.

The influence of the collision-sets upon the velocity of bimolecular thermal reactions was already discussed in a paper by Weiss.¹ The existence of collision-sets tends to slow down the reaction rate; but its influence can become appreciable only if the activation energy is very small—so small that the proportion $1/x$ of the number of collisions in which this energy is attained is greater than $1/\bar{n}$. In this case, the molecules which have to wait \bar{n} times longer than in a corresponding gas for their first collision, are unable to make use (statistically speaking) of all the \bar{n} collisions forming the set, because they react already after the first x collisions. For all bimolecular reactions of which the velocity can be studied experimentally, x is, however, of an order much higher than 10, and no effect of the "intermittency" of collisions can therefore be observed, at least in ordinary non-viscous solutions. In highly viscous systems the reaction velocity can be expected to decrease because of an effect of this kind.

A process in which the influence of the intermittent character of the collision-mechanism is very important is the quenching of fluorescence in liquids, because this reaction often occurs at the very first collision of the activated molecule with an appropriate partner. Wawilow and Franck² have discussed the problem of the quenching of fluorescence in solution and the influence of the viscosity from this point of view, connecting the efficiency of the quenching to the time which the quenching molecule needs to diffuse towards the activated molecule. The problem of the coagulation of sols by electrolytes was earlier treated in the same way by Smoluchowski.³ In both these cases the essential problem can be formulated as follows. At the beginning of an interval, the particles are distributed at random; how long would it take them to collide for the first time? In this paper, we are interested also in another side of the problem: supposing that the molecules are in a state of collision at the beginning of an interval—how long would it take them to reach a random

¹ J. Weiss, *Naturwiss.*, 1935, 23, 229.

² S. I. Wawilow, *Z. Physik*, 1929, 53, 665; J. M. Franck, S. I. Wawilow, *ibid.*, 1931, 69, 100.

³ Smoluchowski, *Physik. Z.*, 1916, 17, 594.

distribution? The case of "photochemical equilibrium" which is discussed in the next section, is one in which both sides of the intermittent collision-mechanism play an important rôle.

(2) The Primary Photochemical Process in Solution.

Atoms or radicals formed by photochemical dissociation in solution—e.g. by a process $A_2 + h\nu \rightarrow A + A$ —are, immediately after their formation, in the same position as two dissolved particles after a collision. They are in touch with each other and imprisoned in a "cage" of solvent molecules. It was pointed out in a previous paper⁴ that this situation offers the possibility of an immediate recombination of the dissociation products, called "primary recombination" to distinguish it from the "ordinary" recombination of atoms or radicals distributed at random throughout the whole body of the gas or solution. The primary recombination tends to decrease the quantum yield of dissociation below unity. Its occurrence is obviously connected with the intermittent collision mechanism discussed in Part I. If the mean number of collisions forming a set is \bar{n} , then the probability of a molecule-pair separating before a second collision has taken place is $1/\bar{n}$. It is often assumed that free atoms or radicals recombine at their first triple collision in gases, and at the very first collision in a liquid phase. Under these circumstances the probability of a freshly-formed atom-pair escaping primary recombination must be equal to $1/\bar{n}$, and the quantum yield of dissociation $\gamma = 1/\bar{n} < 1$. On the other hand, the intervals between the sets being \bar{n} times longer than the average collision intervals $\theta_{(gas)}$ in a corresponding gas, the mean "expectation of life" of an actually separated atom-pair will be $n\theta_{(gas)}$. The stationary concentration of the free atoms in the illuminated solution is given by the product of the velocity of their production and their mean life-time. The first being proportional to $\gamma = 1/\bar{n}$, and the second to \bar{n} , the concentration itself becomes independent of the occurrence of primary recombination, i.e. of the existence and length of the collision-sets. The kinetics of all photochemical reactions of which the velocity is proportional to the concentration of free atoms is therefore unaffected by primary recombination, and no hints as to the amount of primary recombination, can be obtained from experiments in which the stationary concentration of free atoms is measured.

This conclusion is based on the assumption that the state of the atoms or radicals formed by light absorption is not essentially different from that of the same particles meeting accidentally in solution. This is not always the case. In the above mentioned paper⁴ the *kinetic energy* of the dissociation products was considered to be essential. The absorbed light practically never exactly corresponds to the convergence limit of the band spectrum. The dissociation products possess therefore a kinetic energy in excess of the average thermal energy at room temperature. We suggested that this excess-energy makes the photochemical dissociation "explosive" and permits the products to break through the surrounding "walls" of the liquid and thus escape recombination. According to the law of conservation of momentum, however, this reasoning is correct only for the case of the dissociation products being heavier than the molecules of the solvent. Otherwise, the dissociation products, however high their kinetic energy may be, are stopped or reflected back by the first collision with a molecule of the solvent. A dependence of the primary recombination upon the amount of excess

⁴ J. Franck, E. Rabinowitch, *Trans. Faraday Soc.*, 1934, **30**, 120.

energy—i.e. upon the wave-length of the absorbed light—may thus be expected especially in the case of solvents with very light molecules—for instance, water. As a matter of fact, a strong dependence of the quantum yield on wave-length is often observed in aqueous solutions.

In the case of a solution of iodine in carbon tetrachloride, however, no such effect of the wave-length can be anticipated, because the mass of the dissociation product ($I = 127$) is less than that of the solvent ($CCl_4 = 156$).

We have already applied this conclusion⁵ to show that neither the absolute value of the stationary concentration of free iodine atoms in illuminated iodine solutions in carbon tetrachloride and hexane, nor their independence on wave-length can be used as an argument against the occurrence of primary recombination in these solutions.

One may think that the excited electronic state $^3P_{\frac{1}{2}}$ of one of the iodine atoms formed photochemically may prevent it from primary recombination. No decrease in the quantum yield was, however, observed at wave-lengths longer than 5000 Å., i.e. in a region where the absorbed energy becomes insufficient to produce an excited iodine atom.

Summary.

1. Under certain conditions the duration of a single collision and the probability of finding two given molecules in a state of collision is the same for two molecules in solution as well as in gaseous state.

2. In this case, the total number of collisions z between dissolved molecules and the average collision interval θ are also unchanged by dissolution.

3. Even in these "ideal" solutions, an important change takes place concerning the distribution of the collision-intervals. *The collisions occur in sets.* The same two molecules collide several times before separating, and this collision-set is followed by a correspondingly longer "inter-set interval."

4. A mechanical model was constructed which shows the rapid increase of the average length of the sets with growing concentration of the particles. It is plausible that in ordinary non-viscous solutions the average length of the sets is of the order of 2 or 3 collisions per set—an estimate which is in agreement with the magnitude of the diffusion coefficients.

5. With average sets of \bar{n} collisions each, the probability of a colliding pair separating before a second collision takes place is $1/\bar{n}$. For atoms or radicals formed by photochemical dissociation in solution, this means a quantum yield of dissociation $\gamma = 1/\bar{n} < 1$. This decrease of the quantum yield by "primary recombination" is, however, exactly compensated by an increase in the mean life-time of free atoms (which is equal to the "inter-set interval"). The stationary concentration of atoms or radicals in an illuminated solution is therefore independent of the occurrence of primary recombination.

6. The kinetic energy of the products of photochemical dissociation can help them to escape primary recombination only if their mass is much larger than that of the molecules of the solvent. This is the case in some aqueous solutions, but not for instance in that of iodine in CCl_4 (which has been the object of our experimental investigations).

Our thanks are due to Professor F. G. Donnan, F.R.S., for the opportunity he gave us to work in this laboratory and for his kind interest in our work.

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University College, London.*

⁵ E. Rabinowitch, W. C. Wood, *Trans. Faraday Soc.*, 1936, **32**, 547.

CATALYTIC INTERCHANGE OF HYDROGEN WITH WATER AND ALCOHOL.

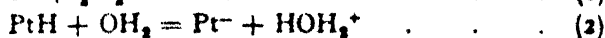
BY D. D. ELEY AND M. POLANYI.

Received 29th May, 1936.

1. Introduction.

In conjunction with the first observation of J. Horiuti and Polanyi of the atomic interchange between hydrogen and water occurring in the presence of platinum black,¹ it was noticed that the addition of acids increased the rate of reaction, while the addition of alkali causes it to slow down.² The effect of alkali is especially pronounced in the atomic interchange between hydrogen and alcohol, the rate of which is reduced four-fold by addition of *N/10* KOH.

Since these effects of the nature of the solution on the rate of exchange were found to be reversible, it was concluded that the nature of the solution was exercising a genuine influence on the rate of atomic interchange and that the rate-determining factor must be one in which hydrogen ions are formed. Assuming that the reaction proceeded in two steps



the authors concluded that it is the second step which determines the reaction rate.

Further results³ supported these considerations, proving (a) that the first order rate (*k*) of interchange in alkaline alcoholic solutions depended on the hydrogen pressure (*p*) as $k \propto \frac{1}{p^{0.5}}$; and (b) that the effect of temperature on the rate corresponds to an activation energy of about 10,000 cal. Both (a) and (b) show that the rate measured is not determined by the diffusion of the hydrogen to the catalyst⁴ and in addition the relationship $k \propto \frac{1}{p^{0.5}}$ seemed to indicate a preliminary equilibrium $\text{H}_2 + 2\text{Pt} \rightleftharpoons 2(\text{PtH})$ to be present corresponding to the first step of the above scheme.⁵

More strength seemed to be added to this conclusion when it was further observed that the inverse proportionality of *k* to the square root of pressure also holds for the enzymatic interchange between hydrogen and water. It was then suggested to measure the rate of the "first step" by the use of the parahydrogen conversion and the $\text{D}_2 + \text{H}_2 = 2\text{HD}$ reaction.⁶

¹ Horiuti and Polanyi, *Nature*, 1933, 132, 819.

² *Ibid.*, 931.

³ Horiuti and Polanyi, *Proc. Manchester Lit. Phil. Soc.*, 1934, 70, 47.

⁴ See discussion, p. 1397.

⁵ A considerable amount of experimental work developing these observations has been carried out in this laboratory by Professor J. Horiuti. We understand that Professor Horiuti will publish these results in the near future.

⁶ Bottomley, Cavanagh and Polanyi, *Nature*, 1935, 136, 103.

The present paper presents some observations carried out on this line, using a mixture of *parahydrogen* and deuterium and following the conversion of the *para*-H₂ and the interchange of the deuterium in the same experiment. A similar technique has been successfully used simultaneously by A. Farkas in a series of catalytic experiments about which a preliminary announcement has been recently made. A. Farkas used *orthodeuterium* and observed the spin conversion and the interchange after the experiment. Two of his observations bear directly on our subject. He found absence of spin conversion when a sample of *ortho*-deuterium was contacted with water containing a platinum catalyst, while at the same time part of the deuterium was replaced by hydrogen. The same result was found with a bacterial emulsion. Farkas concludes from these observations that the atomic exchange is in both cases an ionisation process.⁶

2. Experimental Technique.

The atomic interchange was set up and controlled in the same way as in the earlier investigations of Horiuti and one of the authors.^{1,2,3} Since this technique has not yet been described we will indicate its main points.

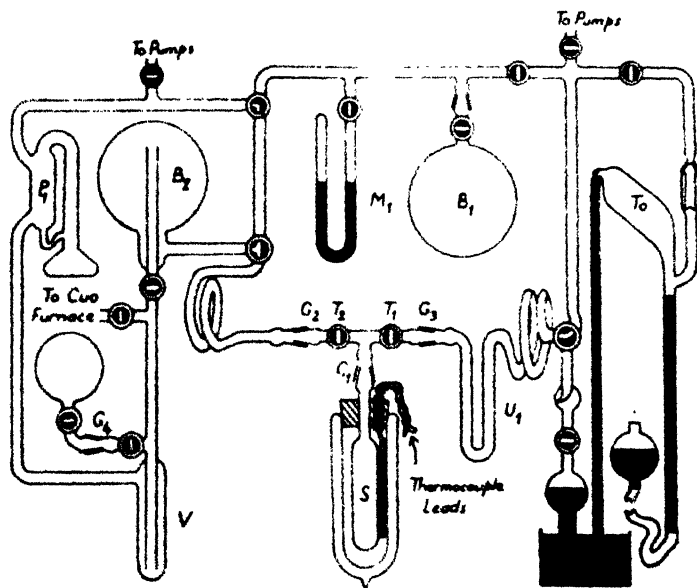


FIG. 1.

A quartz vessel (S in Fig. 1), which, including the tubing up to the taps T₁ and T₂, had a volume of 110 cc., was attached to a vacuum apparatus by two standard ground joints G₁ and G₂, which formed a bearing for shaking the vessel in a plane perpendicular to the paper. The vessel

⁶ We cannot comment on these experiments as we do not know their exact details. However, we would draw attention to the fact that, when the solution is not shaken, there is a strong probability that the diffusion of gas to the catalyst governs the rate. In this event the result reported by Farkas would still be obtained, while it would have no bearing on the true reaction mechanism. We wish to acknowledge the courtesy of Dr. A. Farkas, who, knowing we were engaged in this work, has refrained from investigating the problem any further.

was immersed in a Dewar vessel containing ice, or water the temperature of which was kept constant by a cooling spiral or a heating coil wound around the neck of the vessel S (see Fig. 2). The temperature of the bath was measured by a thermocouple, indicated in Fig. 1.

The platinum catalyst (carefully washed with the solution under examination) was placed in the reaction vessel and 10 c.c. of the liquid (*i.e.* water or alcohol or a solution made up with these liquids) was added. The system being then evacuated the mixture of para-hydrogen (in the earlier experiments, normal hydrogen) and deuterium was introduced from the storage bulb B_1 , by means of the Toepler pump T_1 through the liquid air trap U_1 , and the total pressure read on the manometer M_1 . The vapour pressure of the liquid was subtracted from this reading to give the pressure of hydrogen in the reaction vessel. The shaking was done by the pull of

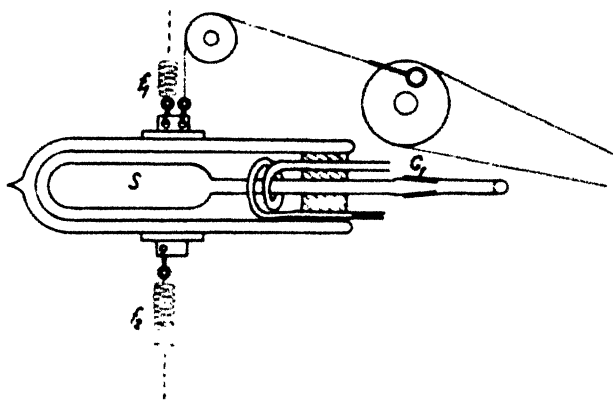


FIG. 2.

a string from a motor-driven eccentric, the usual frequency of 15-20 vibrations per second being controlled by the tension in the springs f_1 and f_2 , which were fixed to a frame. The hydrogen was introduced through tap T_1 after steady shaking had been reached, the letting-in of the hydrogen taking only about three

seconds. A similar time was required to remove the greater part of the hydrogen through T_1 by means of the diffusion pump P_1 into the evacuated three-litre bulb B_2 . The gas was then circulated through the liquid air trap V by means of P_1 for thirty minutes to remove all traces of vapour, and then either burnt in a copper-oxide furnace or expelled into an evacuated bulb attached to the ground-joint G_1 . In the first case the water so obtained was distilled and analysed for deuterium by the micropycnometer method⁷—(this was the procedure in the earlier experiments not using parahydrogen);—in the second case the bulb was removed to the thermal conductivity apparatus and analysed by the method of A. and L. Farkas for para-hydrogen and deuterium content.⁸ Some practical modifications of this method which were used in the measurements are described in a supplementary paper by Eley and Tuck.⁹

3. Preparation of Materials.

Ethyl Alcohol.—The aldehyde was removed by refluxing with KOH, and after distillation it was refluxed with quick-lime. Distillation off fresh quick-lime gave alcohol with less than 0.3 per cent. water content.

Hydrochloric Acid.—I.C.I. chemically pure HCl was diluted and twice distilled, the constant boiling mixture so obtained being diluted as required.

Caustic Potash Solutions.—Merck's pure KOH was used.

⁷ Gilfillan and Polanyi, *Z. physikal. Chem.*, A, 1933, 166, 254.

⁸ A. Farkas, *Z. physikal. Chem.*, B, 1933, 22, 344; A. Farkas and L. Farkas, *Proc. Roy. Soc.*, A, 1934, 144, 467.

⁹ See page 1425.

The Para-hydrogen/Deuterium Mixture.—99 per cent. D_2 gas obtained by electrolysis of alkaline D_2O , was diluted with cylinder H_2 until it was about 4 per cent. in deuterium content and, after purification by passing through a heated palladium thimble, it was treated with active charcoal at the temperature of liquid air, to bring about a *para*- H_2 shift in the usual way.¹⁰

Platinum Black.—In all the experiments (with one exception noted in the tables: catalyst III) this was prepared by reduction of H_2PtCl_6 with

TABLE I.

Expt.	Date.	t in min.	k_D in min. ⁻¹
0.03 gm. Pt black (Ia), 10 c.c. aqueous 0.1 N HCl. Partial Pressure of H_2 = 140 to 156 mm. Temp. = 0° C.			
1	9. 11. 34	30	0.022
2	"	30	0.025
3	"	42	0.022
4	"	30	0.022
5	"	30	0.021
6	"	30	0.024

TABLE II.

Expt.	Date.	Partial Pressure of H_2 , mm.	t in min.	k_D in min. ⁻¹
0.03 gm. Pt black (Ia), 10 c.c. aqueous 0.1 N HCl. Temp. = 0° C.				
7	24. 11. 34	142	30	0.024
8	"	313	30	0.013
9	"	300	30.5	0.009
10	"	35	30	0.076
11	"	35	30	0.069
12	"	30.5	30	0.060
13	"	286	30	0.012
14	"	145	30	0.027

formaldehyde, according to Houben-Weyl II (*Zweite Auflage*), p. 496. One gram of $PtCl_4$ at a time was so treated and the platinum black so obtained was divided up by pipetting its suspension in water. One-sixteenth of the yield was the quantity usually used in the exchange experiments, and according to calculation it equals 0.3 gm., assuming the yield equals 100 per cent. The pipetting method was found to give a moderately accurate division of the platinum black.

The conditions under which the various experiments have been conducted are given in the Tables. The Roman numerals I, II, etc., refer to the "batch" of catalyst (obtained from 1 gm. $PtCl_4$), while the small letters *a*, *b*, etc., refer to particular specimens obtained by subdivision of the batch. Care has been taken in the investigation of all effects of pressure, temperature, etc., to keep check on the activity of the catalyst by inserting experiments under a fixed set of conditions between individual members of a series under varied conditions. Wherever the catalyst has been "disturbed," *e.g.* in changing from one solution to another, the authors have assured themselves as to the reversibility of the effect by returning to the original system. The order in which the experiments have been done may be seen from the dates given in the tables.

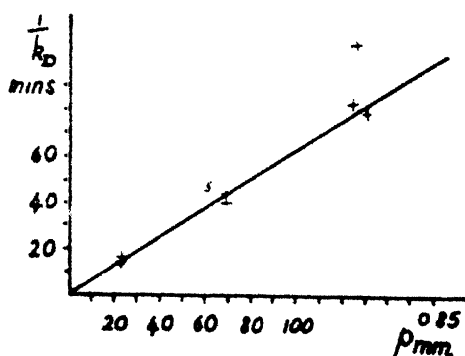


FIG. 3.

¹⁰ Bonhoeffer and Harteck, *Z. physikal. Chem.*, B, 1929, 4, 122.

4. Experimental Results.

In the Tables * the first order velocity constants of the atomic interchange, $k_D = \frac{1}{t} \cdot 2.3 \log \frac{C_0^D}{C_t^D}$ are given in min.^{-1} , and, where *para*-hydrogen

was used, the first order constants $k_P = \frac{1}{t} \cdot 2.3 \log \frac{C_0^P}{C_t^P}$ are also given.

C_0 and C_t are the deuterium (D) or *para*-hydrogen (P) contents at the beginning and end of the experiment, respectively. We proceed in our report by commenting on successive parts of the Tables.

Table I. shows the reproducibility of k_D when the reaction is repeated on one day several times. In Table II. it is shown that k_D increases with decrease of pressure in a manner similar to that shown in earlier experiments with heavy hydrogen and alcoholic potash. The data can be approximated by $k_D \propto \frac{1}{p^{0.33}}$ as shown in Fig. 3.

A brief discussion of the part played by the purely physical processes of dissolution and diffusion in determining the reaction rate might be given here. The rate at which hydrogen is dissolved certainly does not retard the reaction to any noticeable degree since we found that by using a large amount of catalyst (0.24 grm.) the velocity of conversion and interchange could be increased to much higher values than those quoted in the Tables. In two experiments made with aqueous N HCl we found

Partial Pressure of H_2 in mm.	T° C.	t mins.	Per Cent. Shift of $p \cdot H_2$	Per Cent. Shift of D.	k_D min.^{-1}	k_P min.^{-1}
109	0	4	89.5	43.5	0.50	0.14
77	0	8	100	87	-	0.25

TABLE III.

Expt.	Date.	t in min.	k_D in min.^{-1}
0.03 grm. Pt black (Ia), 10 c.c. aqueous 1:1 N HCl. Partial Pressure of H_2 = 140 mm. Temp. = 0° C.			
15	17. 1. 35	30	0.028
16	"	30	0.026
0.03 grm. Pt black (Ia), 10 c.c. aqueous N/10 KOH. Partial Pressure of H_2 = 140 mm. Temp. = 0° C.			
17	24. 1. 35	90	0.0056
18	"	110	0.0058
19	28. 1. 35	93	0.0064
20	29. 1. 35	90	0.0064
21	30. 1. 35	90	0.0057
22	"	92	0.0057
23	4. 2. 35	92	(0.0032)
24	"	90	0.0062
25	"	80	0.0055
26	11. 2. 35	90	0.0062
27	15. 2. 35	90	0.0052

The part played by the process of diffusion of the hydrogen to the catalyst cannot be eliminated completely but our main conclusions are not affected by this uncertainty. Taking constant quantities of catalyst the diffusion rate should not be affected by the HCl or KOH added to the solvent, and the rate expressed in a first-order constant should be independent of pressure while its temperature coefficient should be mainly that of the solubility of hydrogen divided by the viscosity.

It follows that variations found in the reaction rate caused by the addition of HCl or KOH to the solution are due to genuine alterations of the reaction rate and that where the reaction is considerably slowed down, the influence of diffusion will be negligible. It follows further that any variation of k_D or k_P with pressure indicates genuine alterations in reaction rate, and here again, the slower

* In the Tables E_D is the activation energy in calories for the interchange reaction, calculated from the temperature coefficient of the velocity constants according to the equation of Arrhenius. E_P is the same quantity for the *para*-hydrogen conversion.

reactions (*i.e.* those at the high pressure end), can be only slightly influenced by the diffusion process.

If the rate of diffusion were governing the reaction velocity, the constants k_D and k_f would have a small temperature coefficient corresponding to activation energies of 3400 cal. for both water and alcohol. Since the measured activation energies are in excess of these values we may again conclude that the influence of diffusion is not predominant. These arguments could be amplified further, but we feel that, taken in conjunction with the evidence presented in Section 5, they form a safe basis for our later conclusions.

Table III. shows that k_D is about four times smaller in aqueous $N/10$ KOH than in aqueous N HCl.

Table IV. gives extensive evidence on the activation energy of atomic interchange in aqueous solutions.

TABLE IV.

Expt.	Date.	T° C.	t in min.	k_D in min. ⁻¹	
0.03 grm. Pt black (Ia), 10 c.c. aqueous N/10 KOH. Partial Pressure of H ₂ = 142 mm.					
28	1. 2. 35	0	90	0.0064	E_D 4300 cal.
29	"	15.4	30	0.0094	
30	"	0	90	0.0059	
31	7. 2. 35	0	90	0.0073	E_D 4500 ± 600 cal.
32	"	17	30	0.0106	
33	"	17	45	0.0111	
34	"	17	45	0.011	E_D 5000 cal.
35	"	0	80	0.0061	
36	12. 2. 35	0	98	0.0055	
37	"	18.6	45	0.01	E_D 5000 cal.
38	"	18.6	45	0.0097	
39	"	0	90	0.0055	
0.03 grm. Pt black (IIa), 10 c.c. aqueous 1:1 N HCl Partial Pressure of H ₂ = 150 mm.					
40	17. 7. 35	0	30	(0.046)	E_D 7000 cal.
41	"	19.2	15	0.075	
42	"	0	30	0.032	
43	"	18.3	15	0.069	E_D 6100 cal.
44	"	0	30	0.032	
45	18. 7. 35	0	30	0.028	
46	"	18	18.5	0.054	E_D 6200 cal.
47	"	0	30	0.027	
48	20. 7. 35	0	30	0.025	
49	"	17.2	15	0.046	E_D 6200 cal.
50	"	0	30	0.022	
0.03 grm. Pt black (IIa), aqueous 1:1 N/10 KOH. Partial Pressure of H ₂ = 147 mm.					
51	23. 7. 35	0	90	0.0059	E_D 5400 cal.
52	"	17	30	0.0098	
53	"	0	90	0.0051	

of the reaction $H_2 + D_2 \rightarrow 2HD$. We can, therefore, assume that the parahydrogen conversion and the interchange are both due to the same reaction, while attributing the ratio k_D/k_f to the higher rate of reaction of H_2 as compared with HD .

¹¹ Z. physikal. Chem. A, 1934, 168, 313; E. Fajans, Z. physikal. Chem., B, 1935, 28, 239.

TABLE V.*

Expt.	Date.	Partial Pressure of H ₂ , mm.	<i>t</i> in min.	<i>k_p</i> in min. ⁻¹	<i>k_p</i>
0.03 grm. Pt black (IIb) aqueous N/10 KOH. Temp. = 0° C.					
54	26. 11. 35	245	85	0.006	0.011
55	"	245	45	0.004	0.013
0.03 grm. Pt black (IIb), aqueous N HCl. Temp. = 0° C.					
56	29. 11. 35	146	34	0.02	0.047
57	"	54	19	0.029	0.048
58	"	265	44	0.021	0.046
59	"	653	60	0.017	0.05
0.03 grm. Pt black (IIb), aqueous N HCl. Temp. = 0° C.					
60	1. 5. 36	80	20	0.022	0.054
0.03 grm. Pt black (IIb), aqueous N/10 KOH. Temp. = 0° C.					
61	7. 5. 36	81	49	0.0064	0.017
62	"	81	98	0.0055	0.013
0.03 grm. Pt black (IIb), aqueous N HCl. Temp. = 0° C.					
63	8. 5. 36	84	22	0.035	0.087
64	"	86	21	0.017	0.055

* In these experiments a mixture of 6 per cent. HD molecules and about 35 per cent. *p*H₂ was used.

The same conclusion can be drawn from the data of the next section, referring to alcoholic solutions. In the course of these experiments the dependence of the reaction rate on pressure and on temperature has been re-examined, to link up our results with previous experiments and with the extensive unpublished work of Professor Horiuti. We found that our system behaved in a similar manner to those observed previously. The rate observed in alcoholic potash decreases with increasing pressure (Table VI.b), the observations being best represented (Fig. 4) by $k_D \propto \frac{1}{p^{0.6}}$. The activation energy of the interchange reaction (Table VI.c) observed in the same solution gives an average of 8500 cal. which is definitely higher than in aqueous solutions, though somewhat lower than the previously observed value of 10,200 cal.

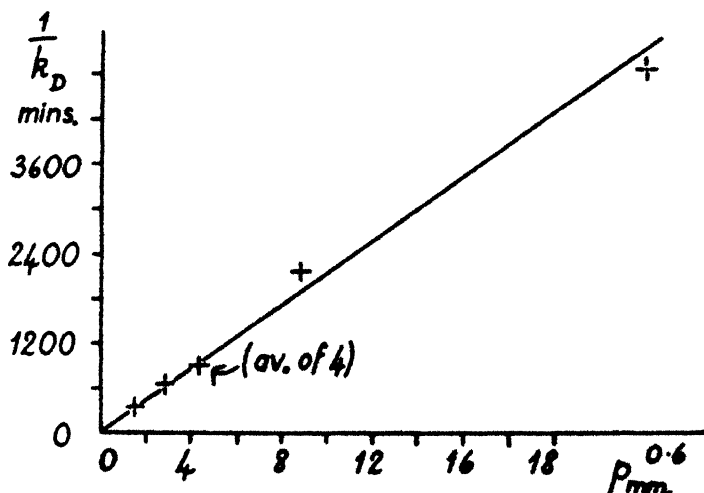


FIG. 4.*

* Note added in proof.—In Fig. 4 the average of Expts. 83, 85, 86 and 91 is taken as $k_D = 0.0011$. Actually it is $k_D = 0.00118$, and the true point is somewhat lower. The correction is within the exptl. error, and does not affect our statement.

In none of the experiments recorded in Table VI. is there an excess of *parahydrogen* conversion over the interchange reactions which goes beyond the factor 2-3 found in aqueous solutions. The ratio k_p/k_D is, indeed, mostly near to unity. We can offer no explanation for the variations of k_p/k_D , some of which might be attributed to experimental errors.

Our main conclusion is that variations in k_p are mainly parallel to variations in k_D , over the whole range of about 100-fold variations of k_D caused by concurrent changes in the nature of the liquid, the pressure and the temperature, and including (in the case of catalyst III in the experiments recorded in Tables VI.b, VI.c) some poisoning of the catalyst. Our present methods cannot be used to follow any wider variations of the reaction rate.

5. Comparison of the Foregoing Results with the Atomic Interchange of Hydrogen with Benzene.

Any suspicion that an actual excess of the rate of *parahydrogen* conversion over the rate of interchange above the normal factor might be concealed by some unknown feature of our experimental technique seems to be removed by the following

TABLE VI. (a).*

Expt.	Date.	Partial Pressure of H ₂ , mm.	t in min.	k _D in min. ⁻¹ .	k _p
0.03 grm. Pt black (IIb), 98 per cent. C ₂ H ₅ OH + 2 per cent. H ₂ O, N/10 KOH. Temp. = 0° C.					
65	10. 5. 36	82	100	0.004	0.012
66	..	82	85	0.0044	0.010
0.03 grm. Pt black (IIb), 100 per cent. C ₂ H ₅ OH (H ₂ O < 0.3 per cent.). Temp. = 0° C.					
67	10. 5. 36	89	15	0.029	0.093
68	10. 5. 36	89	9	0.029	0.038
0.06 grm. Pt black (IIc), 98 per cent. C ₂ H ₅ OH + 2 per cent. H ₂ O, N/10 KOH. Temp. = 0° C.					
69	1. 12. 36	178	16.5	0.016	0.013
70	..	181	35	0.009	0.019
71	..	176	97	0.008	0.013
72	..	20	12	0.029	0.022
73	..	185	52	0.014	0.014
0.03 grm. Pt black (III), prepared by reducing PtO ₂ with H ₂ gas). 100 per cent. C ₂ H ₅ OH. Temp. = 0° C.					
74	5. 2. 36	135	70	0.0057	—
75	..	147	70	0.0057	—
0.03 grm. Pt black (III), 98 per cent. C ₂ H ₅ OH + 2 per cent. H ₂ O (water added by pipette, vessel immediately pumped out). Temp. = 0° C.					
76	10. 2. 36	147	41	0.0027	—
77	..	147	54	0.0027	—
0.03 grm. Pt black (III), 100 per cent. C ₂ H ₅ OH (from fresh batch : † catalyst well washed). Temp. = 0° C.					
78	10. 2. 36	149	80	0.086	—
79	..	149	96	0.078	—
80	19. 2. 36	127	10	0.068	0.196
0.03 grm. Pt black (III), 98 per cent. C ₂ H ₅ OH + 2 per cent. H ₂ O. Temp. = 0° C.					
81	19. 2. 36	115	41	—	0.09
0.03 grm. Pt black (III), 98 per cent. C ₂ H ₅ OH + 2 per cent. H ₂ O + N/10 KOH. Temp. = 0° C.					
82	20. 2. 36	115	71	0.0034	0.0077

* In these experiments a mixture of 6 per cent. HD molecules and about 35 per cent. *p*H₂ was used.

† The large (12-fold) increase in velocity constant observed here appears to be due to activation of the Pt black on admission of air. It would appear that the reduction of PtO₂ by H₂ at 200° C. has yielded a preparation less active than that obtained by HCHO. This action of air is borne out by the fact that admission of air to Pt black (prepared with formaldehyde) often leads to a transient increase in catalytic activity.

observations on the system $H_2 + 0.03$ grm. Pt black (IIb) + 10 c.c. benzene.¹² In two experiments we found:—

Partial Pressure of H_2 in mm.	$T^\circ C.$	t mins.	k_p	k_D
47	19	32	0.079	0.0029
120	19.5	12.5	0.065	0.0024

The *parahydrogen* conversion is found to go 20-30 times as fast as the interchange. This result confirms the assumption made previously¹² that the dissociation of H_2 into atoms is faster than the interchange with benzene. At the moment we only wish to emphasise the fact

that we have here obtained a considerable excess of *parahydrogen* conversion over the interchange reaction, thus proving that our experimental procedure does detect an excess when it is present.

TABLE VI. (b).*

Expt.	Date.	Partial Pressure of H_2 , mm.	t in min.	k_D in min. ⁻¹	k_p in min. ⁻¹
0.03 grm. Pt black (III, somewhat poisoned), 98 per cent. $C_2H_5OH + 2$ per cent. H_2O , $N/10$ KOH. Temp. = $6^\circ C.$					
83	12. 3. 36	35	127	0.00136	0.00176
84	" "	120	380	0.000456	0.000805
85	13. 3. 36	35	207	0.00111	0.00117
86	10. 3. 36	35	321	0.00119	0.00117
87	" "	18	189	0.00152	0.00119
88	18. 3. 36	639	707	0.000207	0.000274
89	19. 3. 36	6	78	0.00279	0.00137
90	20. 3. 36	21	228	0.00126	0.000985
91	20. 3. 36	35	225	0.00108	0.00076

Discussion.

We restrict ourselves to a quite provisional statement of the theoretical implications of our results, because other lines of investigation carried on in this laboratory, especially by the use of polarised metal surfaces, indicate that the phenomenon of ionisation is too complex to be interpreted on the evidence of our experiments only.

TABLE VI. (c).*

Expt.	Date.	Partial Pressure.	$T^\circ C.$	t in min.	k_D in min. ⁻¹	k_p in min. ⁻¹	
0.03 grm. Pt black (III, somewhat poisoned), 98 per cent $C_2H_5OH + 2$ per cent. H_2O , $N/10$ KOH							
92	23. 3. 36	41	20	173	0.00282	0.00307	$E_p \approx 8800$ cal. † $E_D \approx 8000$ cal.
93	" "	39	22	201	0.00266	0.00381	
94	" "	34	0	216	0.00086	0.00142	
95	26. 3. 36	109	19.25	261	0.0012	0.0026	$E_p \approx 9500$ cal. $E_D \approx 9000$ cal. ± 500 .
96	" "	109	0	915	0.00029	0.0008	
97	" "	109	18.2	243	0.0011	0.0026	
98	" "	109	0	650	0.00036	0.0009	

* In these experiments a mixture of 6 per cent. HD molecules and about 35 per cent. pH_2 was used.

† For the calculation of E_D and E_p expt. 91 was used in addition to the expts. in Table VI. (c).

¹² Compare Horiuti, Ogden and Polanyi, *Trans. Faraday Soc.*, 1934, **30**, 663.

¹³ Horiuti and Polanyi, *Trans. Faraday Soc.*, 1934, **30**, 1164.

Since the rate of *parahydrogen* conversion is 2-3 times in excess of the interchange rate between HD and water or alcohol we assume that the conversion is essentially the same process as the interchange, the rate being somewhat higher because H_2 reacts more quickly than HD. There is no evidence of a preliminary equilibrium $H_2 \rightleftharpoons 2H$ corresponding to the "first step" in the mechanism quoted in our introduction. In consequence, the rate-determining process must be the splitting of the H_2 molecules. This splitting is influenced by the nature and acidity of the liquid, which leads us to the conclusion that the products of the H_2 dissociation (or, more exactly, the transition state leading to them) are profoundly influenced in their energy by electrostatic interaction with the ions of the liquid. These products, therefore, cannot be homopolar H atoms but must be H ions or alternatively H atoms in a strongly polarised state, *e.g.* participating in a strongly polar Pt—H bond.

The previous interpretation of the pressure dependence $k_D \propto \frac{1}{p^n}$ where n is about 0.5 can no longer be upheld. This function should be explained as resulting from the adsorption isotherm of the H_2 molecules (or, more accurately, of the molecules in the transition state) and not as the equilibrium constant of the reaction $H_2 \rightleftharpoons 2H$.*

Finally, it is interesting to note the relationship between reaction rate and activation energy when comparing N HCl and $N/10$ KOH solutions, in water. The reaction rate in the former is about 4 times greater than in the latter, while the activation energy is about 1600 cal. smaller for the slower reaction. The variation in the reaction rate is thus seen to be dominated by the changes in the temperature independent factor. A similar effect has been observed by Professor Horiuti for the addition of KOH to 98 per cent. $C_2H_5OH + 2$ per cent. H_2O .

* Reference should be made to the recent paper of J. Horiuti and G. Okamoto (*Scientific Papers of the Institute of Physical and Chemical Research of Japan*, 28, 231), which contains a preliminary report on interchange reactions catalysed by an anodically polarised nickel sheet and details of measurements of the electrolytic separation factor of H and D on cathodes consisting of various metals. Horiuti suggests some new concept of the processes involved, which we will discuss at a later stage of this enquiry.

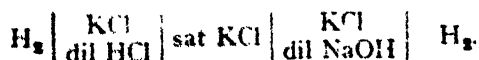
THE ELECTROLYTIC DISSOCIATION OF HEAVY WATER.

By W. F. K. WYNNE-JONES.

Received 8th June, 1936.

In a preliminary communication¹ it was reported that the ionic product of heavy water is about one-third that of ordinary water: the work has now been brought to a conclusion and the revised value for the ratio is $1/5$.

The method employed is to measure the e.m.f. of cells of the type



¹ Topley and Wynne-Jones, *Nature*, 1934, 134, 574.

Such cells of course give rise to a liquid junction potential, but the uncertainty of this is not sufficient to make the results unreliable and there is much evidence that when the liquid junction is properly controlled data obtained by this method agree excellently with those from methods which have the theoretical advantage of avoiding liquid junctions. As Guggenheim² has pointed out, the e.m.f. of a cell with liquid junction can be written

$$E = E_{\text{El}} + E_{\text{S}} + E_{\text{D}}$$

where E_{El} is the difference of the electrode potentials, E_{S} is a "salt effect" and E_{D} is the diffusion potential calculable by the equations of Planck and Henderson. E_{S} cannot be unambiguously separated from E_{El} but it will vanish at infinite dilution and may therefore be eliminated by extrapolation. In a cell of the type used here both E_{S} and E_{D} are small since the solutions in the two halves of the cell are practically identical.

The greatest difficulty encountered in the work was the preparation of the solutions since the amount of heavy water available, though large for this substance, was insufficient for the use of ordinary volumetric and analytical methods: the method finally adopted was to add weighed amounts of concentrated solutions of acid and alkali in ordinary water to weighed amounts of heavy water.

Since the final concentrations of acid and alkali were small, the percentage of light water introduced by this procedure did not exceed 0.2 per cent.

As it is of interest to compare all the thermodynamic properties relative to dissociation and not merely the free energy change, it was decided to measure the temperature coefficient of the dissociation constant and measurements were made at 15°, 25° and 35°.

Experimental.

The electrical equipment consisted of a Queen potentiometer with which readings could be made directly to 0.02 millivolt, a Leeds and Northrop high sensitivity galvanometer of 570 ohms resistance, and a standard cell which was repeatedly checked against a set of standards belonging to Professor G. A. Hulett. The apparatus was all placed on an equipotential shield as recommended by White.³ The potentiometer was calibrated by the makers and checked during the course of the work.

Three thermostats were used and the temperatures which were constant to 0.01°, were read on thermometers which had been originally calibrated at the Physikalische Reichsanstalt and rechecked at the Bureau of Standards; the ice points of these thermometers were determined during the course of this work and the appropriate corrections applied to the readings.

The cells were made in one piece with a suitable arrangement of taps so that the liquid junctions could be made in the manner proposed by Unmack and Guggenheim⁴ and without exposure to the atmosphere. Each half-cell contained about 3 c.c. of solution and the liquid junction required about 2 c.c. The cells were of Pyrex glass except for the tubes carrying the electrodes; these tubes, however, did not come into contact with the solutions. It was found possible to make measurements on one cell successively at the three temperatures without the necessity of bubbling hydrogen at each temperature: this was effected by making

² Guggenheim, *J. Physic. Chem.*, 1930, **34**, 1758.

³ White, *J. Amer. Chem. Soc.*, 1914, **36**, 2011.

⁴ Unmack and Guggenheim, *Det. Kgl. Dansk Vid. Selsk.*, 1930, **10**, 8.

the first measurement at the lowest temperature, closing the taps connecting the liquid junctions before transferring to the next thermostat and at intervals momentarily opening the taps connecting the saturated KCl bridge and the hydrogen electrodes to the atmosphere. Cells treated in this way agreed to a tenth of a millivolt with cells equilibrated in the usual way. All cells kept constant in e.m.f. to 0.05 millivolt for at least 1 hour after the liquid junctions were made.

The hydrogen electrodes were made of platinum foil covered with a black deposit according to the instructions of Popoff, Kunz and Snow.⁴ Before a measurement with heavy water the electrodes were dried with filter paper and washed with a few drops of the solution to be used in the cell.

The hydrogen (protium) gas was obtained from a cylinder and was passed through a tube containing active copper at 500°; the deuterium was prepared from pure D₂O in an electrolytic generator which had previously been run for a sufficient length of time to get rid of traces of light hydrogen.

The acid solutions were made up from constant-boiling hydrochloric acid; about 0.01 gm. of acid was introduced into a special flask and sufficient KCl added to make the required ionic strength; about 10 c.c. of heavy water were then distilled directly into the flask and its amount determined by weighing. The alkaline solutions were similarly prepared from a concentrated solution of NaOH which was standardised against the constant boiling acid. In the earlier experiments the acid and alkali were weighed directly in the vessel used for the solutions but it was found to be both quicker and more accurate to use a micro-pipette of the type devised by Linderström-Lang and Holter;⁵ such a pipette can easily be made to deliver 0.01 c.c. with an accuracy of 0.2 per cent.

The heavy water was prepared electrolytically and found by Dr. P. W. Selwood to have a density of 1.1079 at 25°; it was distilled in a current of nitrogen consecutively from alkaline permanganate and barium oxide in an all-glass apparatus, the final distillation being direct into the weighing flask. The density of the water after it had been in use for a month was 1.1070.

Results.

In Table I. the first column contains the value of the ionic strength, the second gives the approximate concentration of acid and base, the

TABLE I.

	μ .	$c_A (\approx c_B)$.	E .	$-\log K + 2.4\sqrt{\mu}$.
H ₂ O	0.1503	0.0008	15° 0.5600	14.521
			25° 0.5587	14.177
			35° 0.5579	13.865
	0.0972	0.0082	25° 0.5603	14.105
			35° 0.5689	13.792
	0.0376	0.0017	15° 0.4937	14.373
D ₂ O	0.1003	0.0057	25° 0.4903	14.029
			15° 0.5990	15.283
			25° 0.5976	14.916
	0.0855	0.0049	35° 0.5968	14.583
			15° 0.5921	15.278
			25° 0.5908	14.913
	0.0422	0.0024	35° 0.5900	14.583
			15° 0.5578	15.201
			25° 0.5554	14.839
			35° 0.5532	14.503

⁴ Popoff, Kunz and Snow, *J. Physic. Chem.*, 1928, **32**, 1056.

⁵ Linderström-Lang and Holter *C.R. Lab. Carlsberg*, 1931, **19**, No. 4.

third the e.m.f. and the fourth the value of $-\log K + 2A\sqrt{\mu}$. The first half of the table gives the results for ordinary water which afford a criterion of the reliability of the method, and the second half gives the results for heavy water.

TABLE II.—IONIC PRODUCTS OF H_2O AND D_2O .

$t^\circ C.$	$H_2O.$	$D_2O.$
15	14.35	15.08
25	14.00	14.71
35	13.69	14.37

In Table II. are given the values of the negative logarithms of the ionic products of H_2O and D_2O at zero ionic strength; these values are obtained by extrapolation and are expressed in

volume concentration units (moles per litre).

Discussion of Results.

For convenience in calculation the concentrations have been expressed as gram-molecules per 1000 grams of solution; for the final values of the ionic product however transposal to volume units has been made by multiplying by the square of the density of water, H_2O or D_2O , at the temperature of measurement. There is usually some ambiguity in the significance of free energy differences when the solvent is changed and Bell⁷ has pointed out that it is impossible to decide the units in which the concentrations should be expressed; here, however, the ambiguity is slight since owing to the virtual identity of the molar volumes of H_2O and D_2O the free energy difference is the same whether the concentrations are expressed in mol. fractions or in volume units.

The values of the ionic product at zero concentration have been obtained by plotting $-\log K + 2A\sqrt{\mu}$ against μ ; K is the ionic product at the ionic strength μ and A is the constant of the Debye-Huckel expression and is equal to $\frac{2.954 \times 10^6}{(DT)^{3/2}} \cdot \sqrt{2d}$. The values of A employed

are given below: for their computation the data of Lewis and Macdonald⁸ for the expansion of D_2O and of Lewis, Olson and Maroney⁹ for the dielectric constants were used.

In Fig. 1 are plotted the values of $\log K$ against $1/T$ and the data of Harned and Hamer¹⁰ for ordinary water are included.

The difference in the slopes of the curves for H_2O and D_2O corresponds to a difference of 940 Cals. in the heats of ionisation of these compounds whereas the difference in their free energy of ionisation is 970 Cals.; it is evident that the entropies of ionisation must be practically identical. If we assume exact equivalence of the changes in free energy and heat of ionisation, we can represent the dissociation constant and the heat of ionisation of heavy water by equations similar to those used by Harned and Hamer, altering only the first term to correspond with the difference in the heats of ionisation of ordinary and heavy water

$$\log K = -4787.3/T - 7.1321 \log T - 0.010365T + 22.801$$

$$\Delta H = 21,926 - 14.812T - 0.04746T^2.$$

⁷ Bell, *J. Chem. Soc.*, 1932, 2905.

⁸ Lewis and MacDonal, *J. Amer. Chem. Soc.*, 1933, **55**, 3957.

⁹ Lewis, Olson and Maroney, *J. Amer. Chem. Soc.*, 1933, **55**, 4731.

¹⁰ Harned and Hamer, *J. Amer. Chem. Soc.*, 1933, **55**, 2194.

These equations are, however, cumbersome in use and necessitate elaborate tables for their accurate application since ordinary temperatures are far removed from the absolute zero; we have therefore preferred to represent our results by the equations

$$\text{H}_2\text{O. } \log K = 14.000 - 0.0331 (t^\circ - 25) + 0.00017 (t^\circ - 25)^2$$

$$\Delta H = 13,450 - 42.8 (t^\circ - 25)$$

$$\text{D}_2\text{O. } \log K = 14.71 - 0.03544 (t^\circ - 25) + 0.00017 (t^\circ - 25)^2$$

$$\Delta H = 14,420 - 42.8 (t^\circ - 25).$$

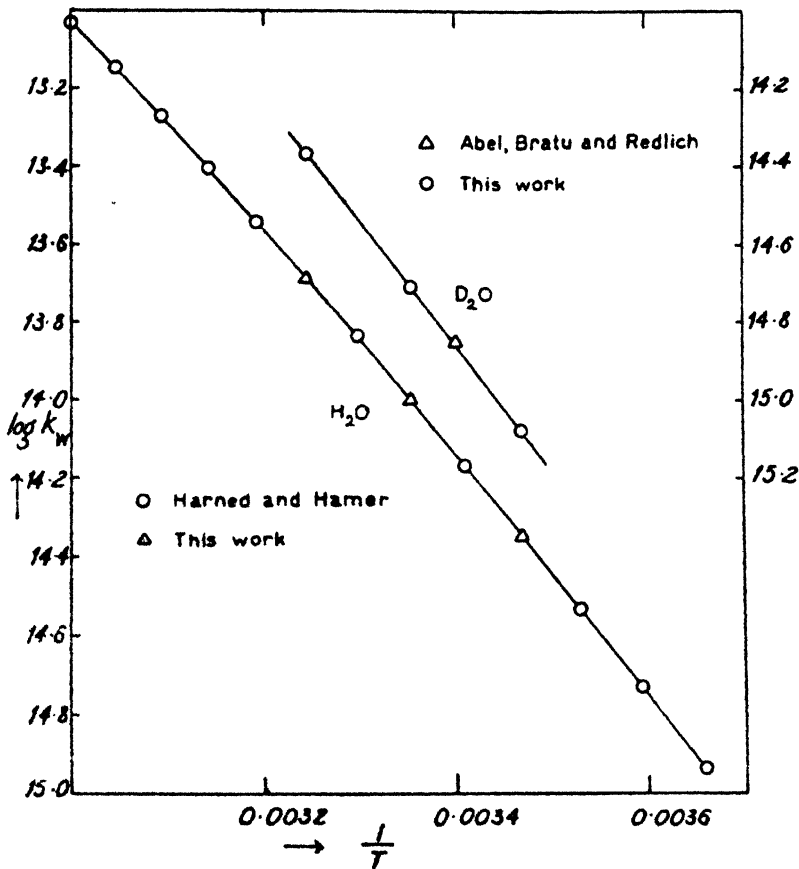


FIG. 1.

These equations are, of course, purely empirical interpolation formulæ but they reproduce the data of Harned and Hamer with an accuracy of about 1 per cent. within the range 0° to 50° C.

It should be noted that the difference in the heats of ionisation of H_2O and D_2O is determined with greater accuracy than would appear from the possible errors in the dissociation constants. This is because the change in the dissociation of water with temperature can be evaluated directly from the temperature coefficient of the acid-base cell without a knowledge of the concentrations, and the liquid junction potentials are substantially independent of the temperature. We are thus able to say that the error in the difference $(\Delta H_{\text{D}_2\text{O}} - \Delta H_{\text{H}_2\text{O}})$ is probably less than 50 calories.

Abel, Bratu and Redlich¹¹ have recently published the results of a determination of the ionic product of heavy water using a cell without liquid junctions. They developed a very elegant micro-technique which enabled them to work with much smaller quantities than were employed in this work. Their results which were obtained mainly at 21° refer to mixtures of H₂O and D₂O and by extrapolation they de-

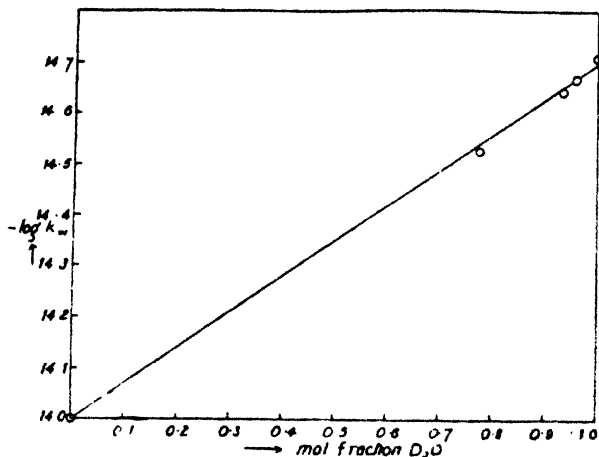


FIG. 2.

duced that the ratio of K_w for H₂O and D₂O is 6.27: on the assumption that the ratio is the same at 25° their value of K_w for D₂O at 25° would be 1.6×10^{-15} ; however, their results are expressed in molalities and in order to convert to the volume concentration scale we must multiply by $(1.1079)^2$, i.e., 1.227; their value

then becomes 1.96×10^{-15} , in excellent agreement with ours.

In Fig. 2 are shown the data of Abel, Bratu and Redlich for mixtures of H₂O and D₂O. The ionic equilibria in these mixtures are quite complicated since there are two forms of hydroxyl ion, three forms of water and four of the hydroxonium ion; nevertheless the almost linear relationship between $\log K_w$ and the mol. fraction of heavy water suggests that the energies of ionisation form an arithmetic series.

Summary.

The dissociation of heavy water has been determined from measurements of electromotive force at 15°, 25° and 35°. At 25° the ionic product of heavy water is 1.95×10^{-15} while that of ordinary water is 1.0×10^{-14} . From the temperature coefficient the heat of ionisation is calculated to be 940 calories greater than that of ordinary water and this difference exactly accounts for the difference in the ionic products.

This work was carried out at Princeton University, New Jersey, and was begun in collaboration with Mr. B. Topley of University College, London: unfortunately, owing to Mr. Topley's departure from Princeton, the work had to be completed without the advantage of his co-operation. The inception of the work was due to him and his help in the early stages was invaluable.

I also wish to express my thanks to Professor H. S. Taylor, F.R.S., for his great kindness in placing the resources of the Frick Chemical Laboratory at my disposal, and to the Leverhulme Trustees for the award of a fellowship.

The University,
Reading

¹¹ Abel, Bratu, and Redlich, *Z. physik. Chem.*, 1935, 173, 353.

MIGRATION OF CAESIUM ON TUNGSTIC OXIDE.

BY L. FRANK.

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§ 1. Introduction.

There has recently been much investigation of the photo-electric properties of monomolecular films of alkali metals on semi-conducting surfaces (such as oxides, salts, etc.), but comparatively little is known about the adsorption process itself. Though this adsorption may of course differ widely for different bases and alkali metals we might expect to find some features of a general nature, the differences being more or less quantitative.

The starting-point of this paper was an observation made in this laboratory, that a surface of iron oxide as is used in a Kunsman source became photo-electric when bombarded with caesium atoms and that the total photo-electric effect decreased with time after cessation of the bombardment. Various reasons might be ascribed as the cause of this decay, *e.g.*, the deposition of layers of gas on the surface, or the re-evaporation of the alkali metal; this paper shows, however, that this phenomenon can only be satisfactorily explained on the assumption of a migration of the caesium into the mass of the oxide. This adsorption is here investigated in some detail.

A similar process of migration has been suggested by Bosworth¹ to explain the decline in the photo-electric effect of sodium and potassium layers on tungsten, and it is not surprising to find that, in our case too, the process takes an appreciable time at room temperature. Bosworth found that the tungsten strip he employed did not act as continuous substrate but had a large capacity for sodium, due, he suggests, to cracks and imperfections which give the metal a sponge-like structure and permit the diffusion of the alkali metal into the body of the strip. Thus, the effective area for adsorption is many times the geometrical surface of the strip. We should expect a surface of tungstic oxide to be even more sponge-like than a strip of tungsten; indeed Powell and Mercer² were compelled to assume such a structure in order to explain their results on the positive ion emission from indium and thallium layers on tungstic oxide. These authors, however, found that little migration into the oxide took place below 400° C.

This work deals with the adsorption of caesium on tungstic oxide as prepared by Powell and Mercer.² This oxide was found to be more convenient to handle than iron oxide, upon which preliminary observations were made and it gives very similar results.

The photo-electric effect is taken as a measure of the concentration of caesium on the outermost surface of the oxide.

¹ Bosworth, *Proc. Roy. Soc., A*, 1935, **150**, 58; 1936, **154**, 112.

² Powell and Mercer, *Phil. Trans.*, 1935, **235**, 101.

§ 2. Preliminary Experiments.

An oxidised tungsten strip (1 mm. wide, 0.07 mm. thick) was bombarded with caesium atoms from a molecular gun, arranged so that only the central part of the strip (1 cm. long) was struck by caesium atoms. This part was found to become photo-electrically active, the oxide itself being inactive. The maximum yield was in the ultraviolet region and a mercury arc was therefore used as a convenient light source in all subsequent experiments. A spot of light (2 mm. \times 1 mm.) was focussed on the strip by a quartz lens; it entered the experimental tube through a quartz window. The lamp was moved parallel to the strip and a distribution of the photoelectric effect (as measured by a Compton electrometer) was obtained. This could be regarded qualitatively as a measure of the surface concentration of caesium at the different points. Fig. 1 in which the relative photocurrents are plotted against the length of the filament

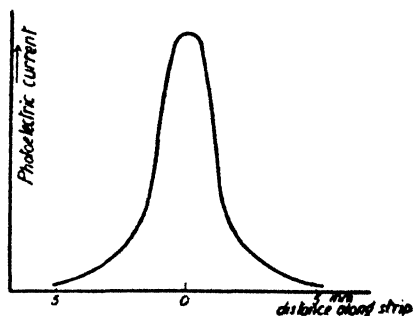


FIG. 1.—Distribution of photo-electric current along the strip.

represents such a distribution at one stage during the bombardment. The photoelectric activity is seen to be restricted to that part of the strip actually struck by caesium atoms.

When the bombardment was stopped the activity was found to decay over the period of hours, as in the experiments of Bosworth. Traversing the strip with a spot of light, however, showed that no appreciable spreading of the patch occurred during the decay, thus proving that this decay was not due to a migration of the caesium over the superficial surface of the oxide.

This process of depositing caesium and letting it decay was repeated many times without removing the caesium that had already decayed, and each time a careful search was made for any spreading effect, which, however, did not occur. The decay could be speeded up by heating the strip, but this also did not produce any spreading of the patch.

It was therefore clear that if the decay was due to an adsorption process it would have to be explained in this case by a migration of caesium into the mass of the oxide. This hypothesis is quite reasonable, because the concentration gradients into the body of the oxide are much steeper than any along the length of the strip. Experience gained during these preliminary experiments led to the construction of apparatus permitting an investigation of the migration over a wide temperature range of the oxide.

§ 3. The Apparatus.

In the final form of the apparatus the caesium atoms are supplied by a molecular gun, so arranged that the beam of atoms falling on the oxide surface could be interrupted at will. A bulb into which caesium had been distilled is shown at the bottom of Fig. 2; it is provided with a pinhole P, 1.5 mm. in diameter, into which a steel ball fits loosely. By controlling the position of the ball magnetically, the atomic beam incident upon the pinhole may, with great efficiency,* be started or stopped instantaneously. The beam is defined by this pinhole and the stop H of 2.2 mm. diameter. By cooling the stop with liquid

* Blank experiments showed that the beam intensity dropped to about one part in 100 within a few seconds after closing the pinhole and to less than one part in 1000 in a few minutes if in addition the oven was removed from the caesium bulb.

air, any scattering or re-evaporation of caesium there is prevented. An intermediate stop S is inserted to prevent excessive accumulation of caesium in the upper part of the gun. This type of molecular gun was first described by Brady.³ The beam then strikes a tungsten strip F (1 mm. wide and 0.07 mm. thick supported on heavy copper leads L, passing into the tube on copper-pyrex seals) which can be heated electrically or cooled by immersing the copper leads in liquid oxygen. Any temperatures above 125° K. can thereby be attained. The temperature of the strip is determined by a Pt-Pt Rh thermocouple (gauge 48) spot-welded to the centre of the strip. The strip is surrounded by a cylindrical nickel electrode E, slotted parallel to its axis, to admit light and also the caesium beam. The light enters the tube through a small quartz window W, stuck on the pyrex flange with stove enamel and baked in air at 220° C. before assembly. A platinised guard ring R, provides electrostatic shielding for the tube. The outside is shielded by covering with earthed tinfoil.

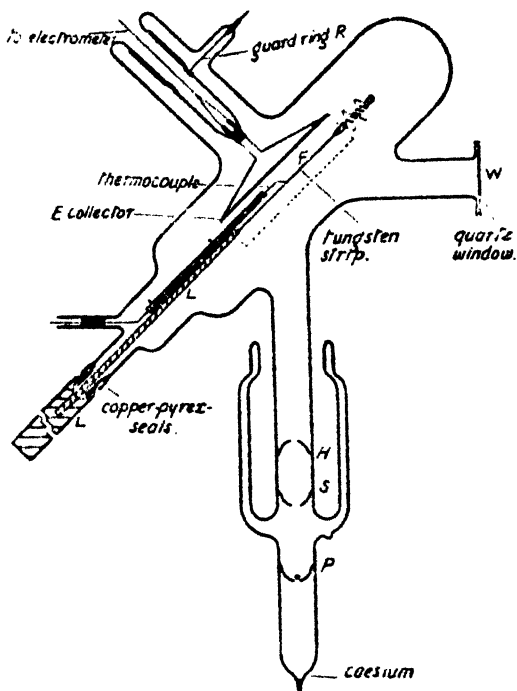


FIG. 2.—Apparatus.

A platinised guard ring R, provides electrostatic shielding for the tube. The outside is shielded by covering with earthed tinfoil.

§ 4. Preparation of Caesium.

Caesium was made (a) from a mixture of caesium chromate and Misch-metal heated by electron bombardment, or (b) by heating a mixture of caesium chloride and calcium in a high vacuum and sealing off into a series of ampoules after repeated distillation. The contents of one of these, broken magnetically, is distilled into the bulb of the molecular gun while the pinhole is closed by the steel ball. No difference was found in the behaviour of caesium from the two sources.

§ 5. Determination of the Beam Intensities.

It is well known from the work of Langmuir and Kingdon⁴ that if caesium atoms strike a hot clean tungsten filament, or a filament which has a monomolecular layer of oxygen on its surface, the atoms will stick for a time and then be re-evaporated as positive ions. The tungsten strips employed here behaved similarly, in spite of their massive coat of oxide. Over the range of beam intensities used a filament temperature of 600° C. was sufficient to ionise all the caesium atoms in the beam, as was proved by the fact that variation of the temperature of the strip on either

³ Brady, *Physic. Rev.*, 1932, 41, 613.

⁴ Langmuir and Kingdon, *Proc. Roy. Soc., A*, 1924, 107, 61.

side of 600° C. made no difference to the ionic current drawn to the collecting electrode.

This observation provided a very convenient and accurate method of measuring the total amount of caesium deposited during a run. The oven temperature was allowed to become steady, the pinhole was opened and the molecular beam allowed to fall upon the red-hot strip. The total number of atoms falling on the strip per sec., n , is given by

$$n = i/10e$$

where i is the steady ionic current in amps. It is then a simple matter of geometry to calculate the number of atoms/cm.²/sec. at the point where the observations of the photo-electric effect are made.

If caesium atoms are allowed to fall on the strip, the total amount deposited can be determined by flashing it to a high temperature and plotting positive ion current against time. By graphical integration of this curve the total quantity of electricity emitted by the strip is obtained and thence the total number of positive ions emitted. From the work of Langmuir and Kingdon, and of Powell and Mercer ² we should not expect any emission of neutral atoms of caesium from the strip for low concentrations of caesium at strip temperatures below those at which there is no detectable ionic current. In agreement with this it was found that within the limits of experimental accuracy, the total amount of caesium deposited on the strip in any experiment was equal to the amount which could be re-evaporated by the method just described. This was true for all concentrations of caesium employed, the total number of atoms deposited varying from 10^{14} to 10^{16} atoms/cm.² at all temperatures at which the decay phenomena were studied (below 130° C.).

It is clear then that no re-evaporation of caesium atoms from the surface occurs at the temperatures at which the decay phenomena are studied.

We have, thus, two alternative ways of determining the total amount of caesium deposited during a given experiment: Either to measure the ionic current produced by allowing a steady molecular beam to fall upon the red-hot oxidised strip and thus deduce the number of incident atoms/cm.²/sec., calculating from this the amount deposited in a given time. Or to remove the caesium at the end of the experiment and estimate the total amount from the integrated emission. The second method was chosen as being the more convenient.

§ 6. Experimental Procedure.

The strip was oxidised as described by Powell and Mercer.² The thickness of the oxide film was of the order of 10^{-4} cm. The apparatus was baked out as well as the presence of the quartz window would permit, all metal parts being thoroughly outgassed. A pressure within the limits 2×10^{-7} to 8×10^{-8} mm. Hg (measured by an ionisation gauge) was obtained in the tube which was continuously pumped out by a mercury diffusion pump through a wide lead and a liquid air trap.

Before performing any experiment the oxidised strip was freed from traces of alkali introduced during manufacture or preliminary handling, since these traces of alkali produce a positive ion emission in addition to that due to the incident beam of caesium atoms. The strip was therefore glowed at 700° C. and a potential of 60 volts applied between it and the collector, so as to eliminate the contaminating ions, the treatment being continued until the thermionic emission from this cause was immeasurable. An ampoule containing caesium was broken and the caesium distilled into the bulb from a side tube (not shown) while the pin-hole was closed. The side tube was then sealed off and the caesium distilled on to the strip by surrounding the bulb with a cylindrical electric oven. An additional heater wound directly on the glass prevented condensation

of caesium near the pin-hole. The temperature of the oven was measured by a Pt-Pt Rh thermocouple. A spot of light from the mercury arc was focussed on the centre of the strip which was also the centre of the caesium beam.

§ 7. Standard Experiment.

The strip at + 60 volts was first kept at 600° C., a temperature sufficient to keep it clean from caesium. The heating current being then cut off, the strip was cooled to the temperature at which the adsorption was to be studied, while the caesium in the furnace reached temperature equilibrium. After reversing the potential to accelerate photo-electrons towards the collector, the pin-hole was opened and the photo-emission measured during the deposition of caesium as a function of time at a fixed spot of the strip. After a given time the beam was cut off by closing the pin-hole and removing the oven surrounding the caesium bulb. Observations of the now diminishing photo-electric emission were continued. After an appropriate time the field was reversed again, the strip flashed to 600° C., so that the deposited caesium was emitted thermionically and the beam intensity computed by the method given in § 5.

§ 8. Experimental Results.

(a) Deposition at Room Temperature.

Fig. 3 shows two characteristic curves of rise and decay of photo-electric effect.

Curve (a) shows the result of a deposition of 1.6×10^{15} atoms/cm.² in 8 minutes; the effect rises continuously until the beam is cut off, after which it decays to a small fraction within a few hours. Curve (b) is a similar result for a smaller beam intensity; not only is the rise here less rapid but a greater deposit is required to produce the same photo-electric intensity. Moreover the rate of decay depends upon the rate of deposition, though the difference becomes less pronounced as the total time of decay becomes large compared with the time of deposition.

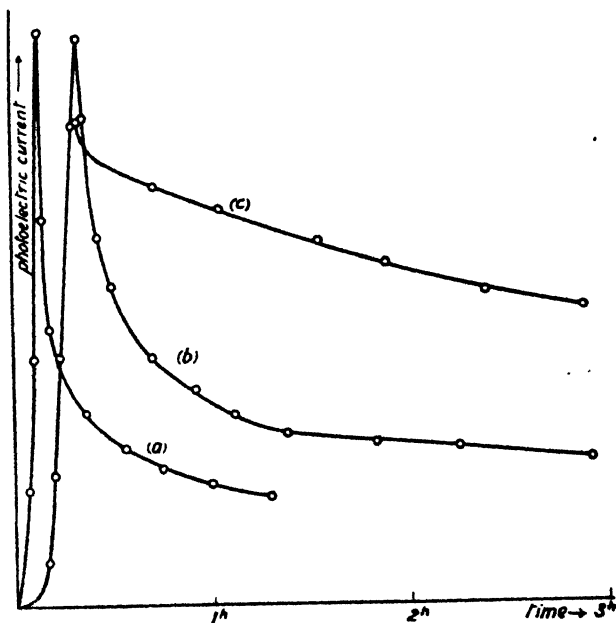


FIG. 3.—Deposition and decay at room temperature.

- (a) Deposition of 1.6×10^{15} atoms/cm.² (3.2×10^{12} atoms/cm.²/sec.).
- (b) Deposition of 2.0×10^{15} atoms/cm.² (1.6×10^{12} atoms/cm.²/sec.).
- (c) See page 1410.

(b) Deposition at 125° K.

At this low temperature, curves of the type of Fig. 4 are obtained, illustrations for different quantities being shown. The decay is very much slower at this temperature, though not completely arrested.

(c) Relation Between Photo-effect and Surface Concentration.

As the decay of the photo-effect with the strip at 125° K. is slow compared with the

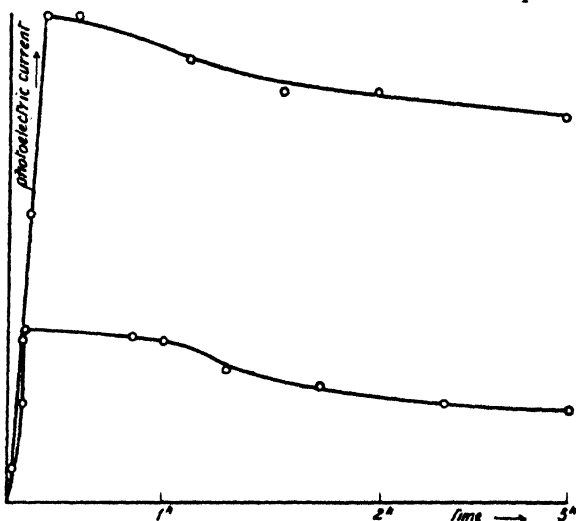


FIG. 4.—Deposition and decay at 125° K.

when the light from the mercury arc was filtered through a glass plate, cutting out all components below 3200 Å. Both curves show marked deviation

from the time of deposition, it is possible to calibrate the photo-current against the surface concentration, as it follows from the above experiments that the migration of caesium into the mass of the oxide can be neglected to a first approximation.

The result of this calibration is plotted in Fig. 5, the upper curve showing the total photo-emission, the lower curve giving the effect

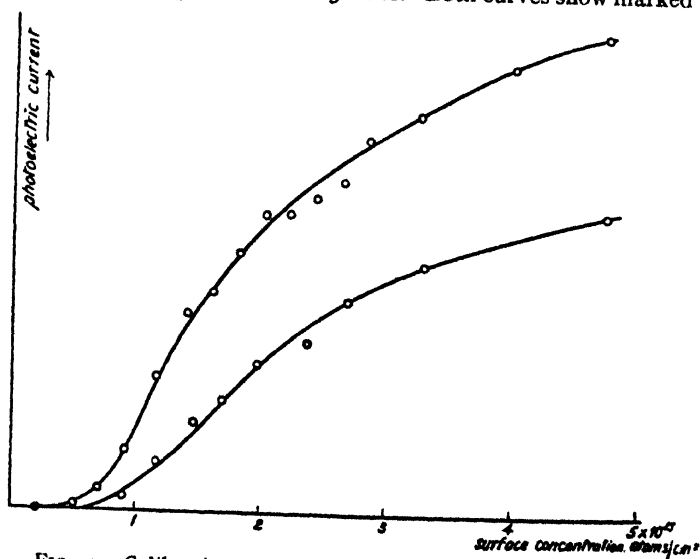


FIG. 5.—Calibration of photo-effect against surface concentration.

tion from linearity for low concentrations and flattening out for concentrations of some 10^{12} atoms/cm.², i.e. a few atomic layers. The latter is in good

agreement with the observations of Brady* who finds that for caesium films on silver the maximum photo electric yield is given by the same order of concentration. From the work of Brady and others it is known that the variation of photo-sensitivity with wave-length depends upon the thickness of the film. The similarity in shape of the curves of Fig. 5 at the high concentrations suggests however that at these thicknesses the sensitivity/wavelength relation has settled down to a standard form. For low concentrations the variation of wave-length sensitivity with thickness must be operative; to this effect we must attribute the relatively flat initial slopes. At any rate we cannot make from these curves any deductions as to the adsorption process with which this work is primarily concerned. Evidence of the spectral distribution does not, of course, show the characteristics of the photo-emission of caesium in bulk, but indicates that we are dealing with an adsorbed layer. In this connection we mention that, while in early rough experiments with iron oxide as base, less than 10 per cent. of the emission was due to light of a wave-length greater than 3200 Å., in the present case up to 60 per cent. is due to this region.

(d) Influence of Adsorbed Layers of Gas.

It is *a priori* very unlikely that a decay (over a period of many hours) of photo-electric emission from a strip kept in thermal equilibrium with the rest of the tube (*i.e.*, at room temperature) could be produced by formation of surface layers of gas; such layers should deposit in a few minutes or even seconds, corresponding to the pressures of 10^{-7} — 10^{-8} mm. Hg after the strip has come to equilibrium. Experiments showed that the photo-electric emission was very sensitive to *changes* in pressure, being lower for higher pressures. Minute traces of gas had a remarkable effect if the strip was at a low temperature (*i.e.*, not at thermal equilibrium with the rest of the apparatus). With the filament at 125° K. such traces would extinguish a high photo-electric effect almost instantaneously or inhibit its appearance during deposition. Indeed in the calibration described under (c) consistency was only obtained by heating the strip to a high temperature while the copper seals were immersed in liquid oxygen, so, as to collect all residual traces on the cold copper leads before cooling the strip itself.

No such difficulties were encountered at higher temperatures; this is consistent with the fact that on warming up the cold strip after deposition had ceased, the photo-emission did not drop immediately but rose sharply at first. The cause of this initial rise due to removal of gas is the reverse of what happens when gas is put on. Clearly, therefore, the phenomenon of decay cannot be attributed to a formation of gas layers and we shall therefore discuss it in terms of migration into the mass of the oxide.

(e) Migration into the Mass of the Oxide.

On this view a certain distribution of caesium will be built up in the oxide during the period of deposition, depending on the intensity of the beam and the temperature of the strip. Curve (a) of Fig. 3 shows a steeper decay than curve (b); the rate of deposition was greater in that case, so that larger concentration gradients were built up. Fig. 6 (a) shows on a larger scale an early portion of the upper curve of Fig. 5, and Fig. 6 (b) shows a deposition curve over the same region of surface concentration, but with the strip at 290° K. In spite of the higher beam intensity in deposition (b), these curves show clearly that a greater total amount of caesium is necessary to produce the same surface concentration at the higher temperature. Fig. 7 shows a similar result for the temperatures 291° K. and 397° K. Very different amounts of caesium may, then, be

accommodated in the oxide, although their surface concentration is the same.

As another illustration, 1.9×10^{18} atoms/cm.² were deposited at 397° K. and, immediately the beam was cut off the strip was allowed to cool to 290° K. and the decay followed. Curve (c) of Fig. 3 which shows the result may be compared with the decay of (b), Fig. 3. The rate of decay is determined partly by the surface concentration and partly by the rate of supply to the surface of atoms from within the body of the oxide. During the deposition at high temperature a greater concentration in depth is set up by the relatively high migration, so that the decay curves (b) and (c) of Fig. 3 are quite different although they were observed at the same temperature and start from nearly the same surface concentration. The film deposited at high temperature, curve (c), decays more slowly, because of the greater store of atoms beneath the surface. These curves provide further evidence against the possibility that adsorbed gas causes decay, since the gas conditions are the same in the two cases.

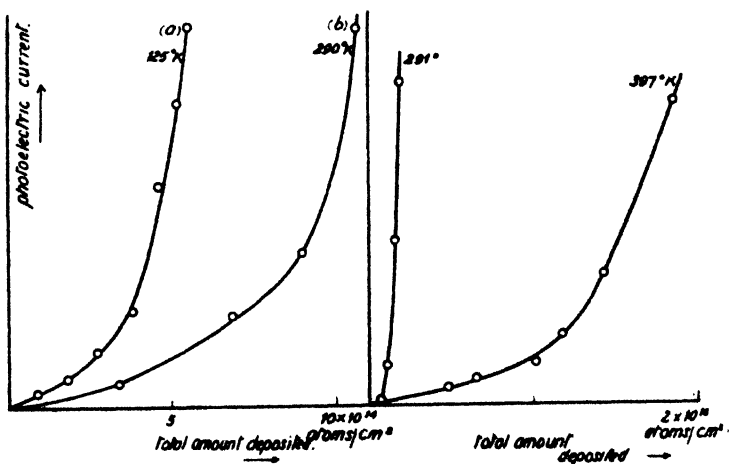


FIG. 6.

Curves of deposition.

FIG. 7.

(f) Measurements of the Activation Energy Associated with the Migration Process.

Picturing the process of migration as one of simple diffusion with a diffusion coefficient D characteristic of the substances involved and of the temperature, but independent of concentration (i.e. assuming that interaction between caesium atoms can be neglected), we have the classical equation

$$\frac{1}{D} \frac{\partial c}{\partial t} = \frac{\partial^2 c}{\partial x^2}$$

where $c(x, t)$ denotes the concentration of caesium in any plane parallel to the surface, at a distance x from it and at the time t .

According to Bosworth¹ the activation energy is given by

$$E = \frac{d \log_{10} \left(\frac{D}{\sqrt{T}} \right)}{d \left(\frac{10,000}{T} \right)} \quad 1.99 \text{ volts}$$

where T is the absolute temperature. Its determination requires a knowledge of the ratio of the diffusion coefficients for different temperatures.

The method finally chosen to determine such ratios of diffusion coefficients is independent of the calibration "photo-effect against surface concentration" of section (c) and of the finite thickness of the oxide. The ratios are determined from the deposition curves (constant beam intensity) making quantitative use of the fact that for a given temperature of the strip the total amount of caesium producing a given surface concentration varies with the beam intensity. Consider two temperatures T_1 and T_2 at which the diffusion coefficient has the values D_1 and D_2 . The boundary conditions for deposition are:—

(1) Oxide, completely free of caesium at the time $t = 0$ (beginning of deposition)

$$c(x, 0) = 0 \text{ for all values of } x.$$

(2) At the actual surface $x = 0$, the concentration depends on the time t as determined by the deposition curve:

$$c(0, t) = \text{given function of } t.$$

Condition (2) can be replaced by another, of which the deposition curve is a consequence, *i.e.*, constant beam intensity n , at which the total amount deposited up to the time t is proportional to t :

$$\int_0^d c(x, t) dx = nt \quad . \quad . \quad . \quad (2a)$$

where d denotes the thickness of the oxide. Taking (1) and (2a) as boundary conditions, (2) is now part of the solution of the differential equation.

This equation, including boundary conditions for the deposition at the temperatures T_1 and T_2 and the beam intensities n_1 , and n_2 , now reads:

$$\begin{array}{ll} (1) & (2) \\ \frac{1}{D_1} \frac{\partial c_1}{\partial t} = \frac{\partial^2 c_1}{\partial x^2} & \frac{1}{D_2} \frac{\partial c_2}{\partial t} = \frac{\partial^2 c_2}{\partial x^2} \\ c_1(x, 0) = 0 & c_2(x, 0) = 0 \\ \int_0^d c_1(x, t) dx = n_1 t & \int_0^d c_2(x, t) dx = n_2 t. \end{array}$$

Now each solution of (1) can be transformed into a solution of (2) by simple reduction of the time scale, owing to the linearity of equation and boundary condition with respect to t . Writing $\alpha\tau = t$ in (2), we obtain

$$\begin{array}{l} \frac{1}{\alpha D_2} \frac{\partial c_2}{\partial \tau} = \frac{\partial^2 c_2}{\partial x^2} \\ c_2(x, 0) = 0 \\ \int_0^d c_2(x, \alpha\tau) dx = \alpha n_2 \cdot \tau \end{array}$$

and c_2 is identical with a solution of (1) if

$$\alpha = \frac{D_1}{D_2} = \frac{n_1}{n_2}$$

and τ is replaced by t . Taking therefore the deposition curves as representations of solutions of the sets (1) and (2) we determine the ratio of the diffusion coefficients D_1/D_2 by determining two relative beam intensities n_1 and n_2 for which the respective deposition curves, taken at the temperatures T_1 and T_2 , coincide when plotted against $n_1 \cdot t$ and $n_2 \cdot t$, *i.e.*, the total amounts deposited on the strip. Examples of deposition curves, plotted against total amount deposited have been discussed in section (e). We now see that in order to find the activation energy from such curves we have to plot "families" of them for different temperatures, varying the beam intensity as family parameter. The ratios can then be computed by interpolation.

In actual practice the range of temperature over which the method is practicable is limited. At low temperatures ($< 250^\circ \text{K.}$) the rate of migration is so slow that a variation of the beam intensity within practicable limits does not produce deposition curves sufficiently distinguishable from each other to allow quantitative conclusions; at high temperatures

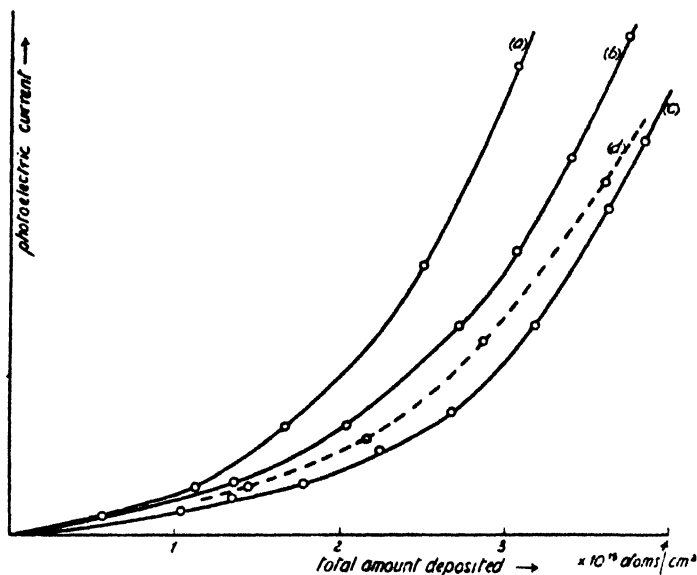


FIG. 8.

- (a) (b) (c) Family of deposition curves at 325°K. for various beam intensities.
(d) Deposition curve at 342°K.

the migration is so fast that very large amounts of caesium are absorbed by the oxide before a reasonable photocurrent is obtained.

Fig. 8 shows three members of the family for the strip temperature 325°K. The dotted curve represents a member of the family belonging to the temperature 342°K. According to the above theory the latter

curve should coincide with one curve of the family belonging to the lower temperature. This however is not the case, and evidently the non-similarity is due to the interaction of caesium atoms during the diffusion process which expresses itself macroscopically in a dependence of the diffusion coefficient on the concentration. It must be remembered that the above treatment neglects this "secondary" effect. The interpolation does not therefore lead to a constant value of the activation energy

TABLE.

Activation Energy in Volts.		Surface Concentration, $10^{14} \text{ atoms/cm.}^2$
334°K.	308°K.	
0.39	0.33	2.4
0.42	0.36	3.3
0.47	0.40	4.2
0.51	0.41	4.8
0.57	0.53	5.3
0.61	—	5.6

for a given temperature; the activation energy appears to rise with the surface concentration (see table). This rise, however, has no significance except that it indicates a breakdown of the above theory for higher values of surface concentration. The surface concentrations are derived from the calibration of section (c).

For a temperature of 250° K. values of the order of 0.2 volts were obtained.

We have so far assumed that the simple diffusion equation governs the process of migration into the oxide. This assumption at best is a very crude approximation, for although undoubtedly caesium leaves the surface and enters the body of the oxide, the oxide may not be homogeneous throughout its depth, the diffusion coefficient may depend upon the concentration of caesium in the oxide, as already pointed out, and in the case of experiments conducted at different temperatures the physical structure of the oxide may suffer reversible changes (*e.g.*, opening or closing of cracks between crystalline aggregates). All these circumstances would cause deviations from the simple theory.

The applicability of the diffusion equation might be tested by depositing instantaneously a certain amount of caesium on the surface of the oxide and following the value of the surface concentration c with time. From the simple diffusion equation, c should then be proportional to $1/\sqrt{Dt}$. This straightforward experiment could not be done, but attempts were made to measure the diffusion coefficient by a method employed by Bosworth.¹ Caesium was deposited on the oxide at a temperature considerably below the temperature at which D was to be measured. The strip was then rapidly heated to the required temperature after the deposition had been stopped. This should provide a close approximation to the ideal boundary conditions postulated above.

However the curves of photo-electric effect so obtained did not show the form to be expected on this simple hypothesis. All showed a much quicker change in the rate of decay (a steep initial fall followed by a very slow final fall) than the theory predicted. No further test of the applicability of the equation was here available, for it was not found possible to determine the diffusion coefficient for migration *along* the strip in the manner employed by Bosworth. Although up to 2×10^{16} atoms/cm² were deposited on the strip, complete saturation with caesium was never attained; even if the decay of photoelectric emission had become very slow at one temperature, it could still always be speeded up by raising the temperature of the strip. One would not, therefore, expect to observe side-ways spreading of the patch, for Bosworth found in his case that saturation in depth had first to be attained before migration along the strip could be detected. We may recall here that Bosworth found the simple theory of diffusion broke down when he was investigating migration along the length of the strip; edgewise spreading of the photo-electrically active patch did indeed occur, but superimposed upon this was a photo-electric emission uniform along the strip. This observation cannot be explained on the simple theory or indeed any obvious modifications of it:

§ 9. Discussion.

A picture of the process we assume as the underlying cause of the phenomena described here is given by Lennard-Jones.⁵ He describes the migration of a substance into another crystalline substance as a diffusion along intercrystalline cleavages, perpendicular to the surface. On such a picture, the migration from the surface into the mass of the crystalline substance will depend on the relation between the size and number of the cleavages and the size of the migrating atoms.

On comparing the results obtained in this paper with those of Bosworth¹ one finds a good agreement between the order of magnitude of the activation energies, so that the general nature of the adsorptive forces is the same for the semi-conducting oxide surface as it is for the metallic tungsten. One also finds a somewhat close qualitative

⁵ Lennard-Jones, *Trans. Faraday Soc.*, 1932, 28, 333.

resemblance between his results for sodium on tungsten and the results presented here. This purely accidental agreement is obviously due to two factors: (1) The tungsten strip used in his experiments has a thickness of 2×10^{-3} cm., while the oxide surface used here is at least 10 times thinner, thus presenting ten times less underlying substance. (2) Probably still more important is the fact that the sodium atom is much smaller than the caesium atom. From the picture presented by Lennard-Jones, and also from a comparison of the experiments of Bosworth on sodium and potassium it follows clearly that the migration of caesium into the metal would be much slower than the migration of sodium. At the same time the migration over the surface would become more appreciable because the caesium atom would have to travel over the surface for a considerable distance before finding an empty gap down which it could slip.*

Bosworth found that the larger potassium atoms were absorbed to a much smaller degree by metallic tungsten than the smaller sodium atoms. If one extrapolates from these to ascertain how caesium would be absorbed by tungsten of a thickness equal to that of the oxide used here, one would find that only about 10^{14} atoms/cm.² (a fraction of a monomolecular layer) would actually be able to diffuse inwards, to fill intercrystalline cleavages. We thus come to the conclusion that the oxide has a far more spongy nature than the metal and an adsorption capacity at least a hundred times higher.

In a recent paper (*Physic. Rev.*, 1936, **49**, 670) Brady and Jacobsmeyer have investigated the photoelectric properties of sodium films on aluminium. They find that the photoelectric emission decays over a short period of time after deposition for films of sodium up to a thickness of 80 atoms and suggest that this decay is due to a re-arrangement of the film which breaks up into globules whereby the effective area is decreased. From the fact that in our case the total amount of caesium deposited can be re-evaporated as positive ions and that there is no evaporation of neutral atoms of caesium even at temperatures at which the vapour pressure of caesium is very high, we conclude that such a formation of globules cannot take place in the experiments described here. It is quite possible that in the case of sodium on aluminium too the photo-electric decay is due to a process of migration into the mass of the metal although the decay does not follow the law predicted by the simple theory of diffusion.

I am greatly indebted to Dr. E. T. S. Appleyard for suggesting the problem and for his constant supervision, to Dr. C. F. Powell and Dr. H. Fröhlich for helpful discussions, and to Professor A. M. Tyndall for placing the facilities of the Laboratory at my disposal. I also wish to thank the International Student Service for a grant.

Summary.

The adsorption of thin films of caesium on a surface of tungstic oxide is studied by a photoelectric method for the temperature range 125° K. to 400° K. The phenomena occurring are described qualitatively by the assumption that the caesium atoms migrate into the mass of the oxide. Values for the activation energy connected with this migration are derived.

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* This migration of caesium over the surface of a tungsten filament has actually been investigated by Taylor and Langmuir (*Physic. Rev.*, 1932, **40**, 463) by a thermionic method. The implications of their results are discussed by Bosworth.¹

THE SWELLING PRESSURE OF ISINGLASS IN WATER AND AQUEOUS SOLUTIONS.

BY H. FREUNDLICH AND P. S. GORDON.

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1. Investigation of the swelling pressure has so far only been carried out for rubber in a number of organic liquids.¹ A disc of rubber, exposed to a measured air pressure, was separated from the liquid by a porous medium; the liquid was imbibed by the rubber, and the ensuing change in its volume was measured under a number of different pressures. Similar experiments with aqueous solutions have not so far been so successful.² The swelling pressure of gelatin could only be determined in this way near the isoelectric point, for in solutions of acids, alkalis, and salts the gelatin was so strongly peptised that it passed through the pores of the membrane before a well-defined equilibrium could be reached. The process of swelling, it should be pointed out, requires a fairly long time—several hours—to reach completion.

Isinglass, though very similar to gelatin,³ has a much smaller tendency to be peptised. Thus while 0.5 gm. of gelatin was completely peptised in 0.1 N NH_4CNS in four hours, a similar quantity of isinglass took at least 10 times as long. This is probably due to isinglass having a very distinct structure. Under the microscope one observes a network of long, curling, fibres. The structure is also seen in a complete dried swimming bladder, for if this hard material is broken the fractured ends have the appearance of asbestos. From it, fibres a few cms. in length may easily be separated. The lack of structure in gelatin may be due to the fact that it is prepared by the prolonged boiling of animal tissue, whereas isinglass is simply dried collagen. When isinglass is brought into solution by heating, and afterwards dried, obvious signs of structure disappear. But as the tendency to be peptised remained smaller than that for gelatin, it seemed hopeful to measure the swelling pressure in water and aqueous solutions by the method just mentioned.

2. The apparatus used (Fig. 1) was very similar to that of Posnjak. The glass portion was made of pyrex glass, the wide tube having a height of 7 cm., a bore of 1.25 cm., while the walls were 1.2 mm. thick. The capillary tube had a length of 70 cm., and a bore of 1.5 mm. The upper metal portion of the apparatus, together with the nut, was of mild steel, but the remaining parts, none of which was used in Posnjak's device, were of "Anka brand" stainless steel. The washers were of vulcanised rubber 1 mm. thick. The porous pots were of dried white china clay. As they had not been fired the material was still quite soft, so that they could readily be shortened to the size desired, namely 1 in. \times 1 in. The

¹ Freundlich and Posnjak, *Kolloidchem. Beih.*, 1912, 3, 517.

² Freundlich and Posnjak¹; v. Terzaghi, *Handb. physik. u. techn. Mechanik*, 1931, IV, 2, 555. The swelling pressure of discs of a sea-alga, *Laminaria*, in water was measured by Reinke (*Hanstein's Botan. Abhandl.*, 1879, 4, 1).

³ The similarity is also shown by the fact that isinglass has practically the same gold number as gelatin; it was 0.0055 mgs., while we found the value 0.01 with the same gold sol and a fairly pure sample of gelatin.

inner surface of each pot was polished with glass paper until smooth, and particular care was taken to have the bottom of the pots, both inside and out, smooth and flat. The space between the porous pot and the glass tube was filled with a cement of yellow litharge and glycerine diluted with water in the proportion of 1 vol. glycerine to 1 vol. water. The cement had initially the consistency of a thin paste, but it set in 24 hours to a hard, porous mass which adhered well to the glass and to the porous pot.

The end of the glass capillary remote from the swelling cell had a copper tube attached with De Khotinsky's cement, and this tube was soldered to a similar tube leading from the air pressure regulating apparatus. The soldered joint could be made or broken in a very short time. Compressed air was stored in a cylinder fitted with a reducing valve. It was led into the apparatus through a needle valve as required, the pressure being released by a similar valve. The pressure was read on a "Standard Test Gauge," made by the Budenberg Gauge Co. A small air reservoir served to minimise the fall in pressure due to any leakage, which proved to be undetectably small over a period of 48 hours.

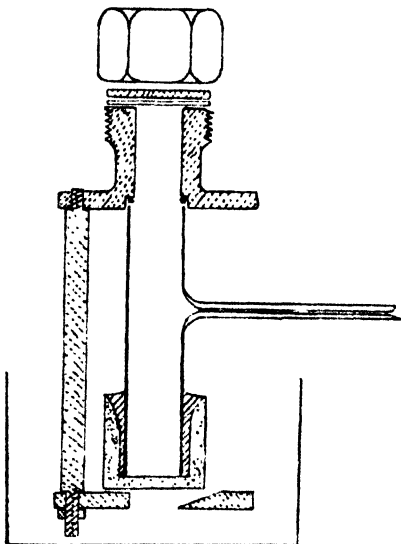


FIG. 1.—Swelling pressure apparatus.

The accuracy of the pressure gauge, and the uniformity of the capillary tube, was tested before use, and it was found that no corrections need be applied. Two small corrections had, however, to be made to the readings to allow for (a) the elastic expansion of the apparatus under increasing pressure, and (b) the change in volume of the mercury filling the apparatus, which, it should be stated, was filled in this manner: a weighed disc of isinglass (ca. 100 mgms.) was forced into the cell until it was in contact with the porous pot, mercury was poured in until it began to overflow and, having removed any air bubbles clinging to the inner surface of the tube with an iron wire, the nut was screwed on firmly. During this process the mercury was prevented from running down the capillary by a small air pressure, the final position

of the mercury in the tube being about 20 cm. from the swelling cell. The correction (a) was determined experimentally each time the apparatus was set up, while (b) was estimated by considering the apparatus to function as a thermometer. The measurements were made in a cellar room in which the temperature did not vary more than $\pm 1^\circ \text{C}$. during the course of an experiment. The correction was $0.25 \text{ cm./}^\circ \text{C}$.

The chief precaution in setting up the apparatus was to observe that no air was left above the mercury, for the elastic expansion of this masked any effect due to the swelling, and also it easily leaked from the cell, with a consequent permanent movement of the mercury in the capillary. Naturally, care had to be taken that no mercury leaked out. Before any readings were taken the pressure in the apparatus was left at 600 gms./sq. cm. for some hours. If the mercury in the capillary moved no readings were taken.

3. The swelling behaviour of isinglass gels was obviously reversible, for the volume was the same whether it was reached from a higher or a lower pressure. The only factor impairing reversibility was a certain

degree of peptisation. This latter was tested by precipitating with tannin the isinglass which had passed into the external liquid. The amount of isinglass could be estimated reasonably accurately from the degree of turbidity produced. In many cases, e.g. in solutions of NaF and NaCl the amount which passed through the membrane was very small. In other cases, e.g., Na_2SO_4 and especially NH_4CNS , the peptisation was much stronger. As long as the amount peptised did not exceed about 10 per cent. a correction could be applied. But in solutions of acids, alkalis, and some salts, the peptisation became so strong that the method did not give trustworthy results.

Let Π denote the swelling pressure, its value being the pressure read on the gauge plus a small amount (60 gms./sq. cm.) due to the head of mercury between the level of the capillary and the level of the isinglass. It is not correct to include the atmospheric pressure in this quantity Π , as the atmosphere bears equally on the surface of the external liquid.

Let γ be the concentration of the gel, i.e., the amount of isinglass in 1000 c.c. of isinglass + liquid.

Then it was shown that the equation $\Pi = \Pi_0 \gamma^k$ also holds for isinglass, Π_0 and k being constants as with Posnjak.¹ The straight lines in the diagrams (cf. Figs. 3-7) show how far this equation agrees with experiment.

It must be emphasised that in swelling pressure we are dealing with a reversible quantity, similar to gas or osmotic pressure. This type of experiment must be sharply distinguished from those in

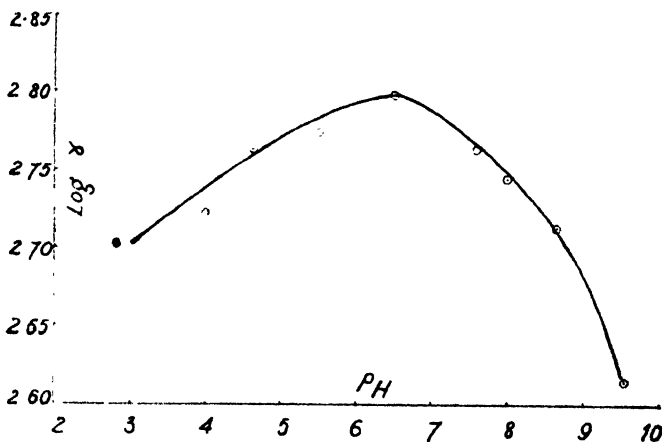


FIG. 2.—Variation of swelling with p_H .

which the maximum of swelling is determined simply by allowing a gel to swell in a liquid without doing any external work. In the latter case we are dealing with an irreversible process similar to the solution of a substance in a liquid.

The reversibility of the swelling is shown by the fact that all the points lie, for any particular case, on the same straight line irrespective of the pressure from which they were reached. (Cf. the line for LiCl in Fig. 3.) Further, the regular linear shape of these curves is not disturbed by the small changes of temperature ($\pm 1^\circ$) which occurred in the period necessary for measuring one of these curves. This shows that small changes of temperature do not cause marked changes in the degree of swelling.⁴

Before entering on details concerning the equation, another point ought to be discussed. As a protein, isinglass is strongly sensitive to changes in the p_H of the solution. The influence of p_H on the swelling of isinglass was investigated in $M/20$ acetate buffers, of p_H between 2.8 and 9.5. In Fig. 2 is shown the variation of the swelling under a constant pressure of 3060 gm./sq. cm. It will be seen that the gel concentration

⁴ This agrees on the whole with the results of Jordan Lloyd and Pleass, *Biochem. J.*, 1927, 21, 1356. Cf. also Northrop and Kunitz, *J. Gen. Physiol.*, 1927, 10, 167.

changes between 410 and 630, with a maximum of gel concentration at a p_H of about 6.5; i.e., there is a minimum of swelling close to the isoelectric point, which was found⁸ to be at about 5.9. This agrees with the results of Chiari,⁶ and Lloyd and Pleass,⁴ that there is a minimum of swelling at the isoelectric point. The small deviation from the value of 5.9 is most probably due to the relatively large buffer concentration; it is well known that ions other than H^+ and OH^- may displace the isoelectric point to a certain degree.⁷

The minimum of swelling at the isoelectric point is not at variance with the maximum of the sedimentation volume of isinglass coated quartz particles at the same p_H , for in the latter case it is the ζ potential of the particles which is decisive.⁶ The amount of isinglass adsorbed is probably so small that the change in volume of the surface layer due to swelling is negligible. The adsorption of isinglass on quartz has not so far been determined, but the extreme similarity between this substance and gelatin renders it practically certain that the adsorption with isinglass is the same as the known adsorption with gelatin.⁹

When comparing the influence of different electrolytes upon swelling pressure we did not fail to take into account the possibility of a p_H change in the solution. Such a change did, in fact, occur. The solution became more alkaline than pure water in solutions of $LiCl$, $NaCl$, KCl , $CaCl_2$, $SrCl_2$, NaI , $NaNO_3$, KIO_3 , Na_2SO_4 , and it became more acid in solutions of $BeCl_2$, $La(NO_3)_3$, NaF ; in $TiNO_3$ solutions the displacement of the p_H was very small, being a little to the alkaline side. The values found are given in Table I.; the changes in p_H , which were measured in every

TABLE I.—COMPARISON OF ELECTROLYTES IN 0.2N SOLUTION.

Electrolyte.	Π at $\gamma = 500$.	k .	p_H .	Peptisation.	Temp. °C.
H_2O . . .	2050	4.7	5.5-6	None	14
$LiCl$. . .	870	2.9	9.5	Slight	17.5
$NaCl$. . .	1445	4.0	8.3	Slight	18.5
KCl . . .	1825	3.8	8.5	Slight	19.3
$TiNO_3$. . .	4170	9.5	6.5	None	13.5
$BeCl_2$. . .	100	7.4	4.5	Strong	18
$CaCl_2$. . .	1530	7.1	8	None	19
$SrCl_2$. . .	2000	7.1	8	Slight	19
$La(NO_3)_3$. .	255	7.8	5.5	Distinct	19
Na_2SO_4 . . .	120	6.3	8.5	Strong	17
NaF . . .	270	5.7	4	Slight	19
$NaNO_3$. . .	2600	5.7	8	Distinct	17.5
NaI . . .	3000	6.2	10	Slight	19
KIO_3 . . .	4170	5.7	8	None	14
NH_4CNS^* . .	5000-6000	(6.2)	8	Very strong	13

* NH_4CNS could not be investigated thoroughly owing to the very strong peptisation observed in its solutions. The equation could not be verified. Hence this value was extrapolated assuming that k was the same as for NaI and choosing the gel concentration where peptisation had been least.

⁶ Freundlich and Gordon, *Trans. Faraday Soc.*, 1935, 31, 915. The high value of the isoelectric point of isinglass compared with the value generally accepted for gelatin (4.7) agrees well with the results of Dubitzkaja and Sokoloff (*Kolloid. Z.*, 1935, 72, 205). They found that the isoelectric point of pure collagen lies above 5 and decreases when the latter is treated with alkalis.

⁶ Chiari, *Biochem. Z.*, 1911, 33, 167.

⁷ For instance Michaelis and Rona, *Biochem. Z.*, 1919, 94, 225; Lloyd and Pleass⁴; Ljalikow, Protass and Fajerman, *C.R. Acad. Sc. U.R.S.S.*, 1935, 1, 615; *Chem. Zentr.*, 1936, 1, 3470.

⁸ Freundlich and Gordon.⁶

⁹ Lindau and Rhodius, *Z. physik. Chem., A*, 1935, 172, 321.

case with a universal indicator, are not of accidental occurrence, for, if the solution was removed and replaced with fresh solution, this rapidly took up the same altered p_H value. If the gel was removed from the apparatus at the conclusion of the experiment and heated until it formed a solution, the p_H of the liquid so formed was found, by the use of the same indicator, to be identical with that of the external solution.

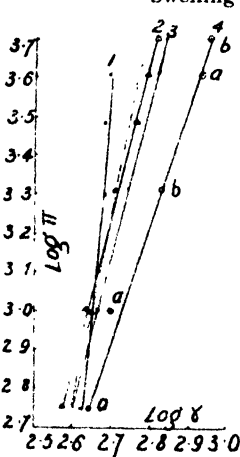
Returning to the discussion of the equation, it was found that the exponent k for isinglass in pure water was slightly larger than the value of about 3 found in the case of gelatin.¹ But gelatin swells more than isinglass: the swelling pressure for a gel concentration $\gamma = 500$ is about 2000 for isinglass and 3000 for gelatin.

Figs. 3-5 and Table I. show that in salt solutions k varies rather strongly—and independently of the change of p_H —according to the nature of the electrolytes. The values found for the chlorides of alkali metals are much smaller than for those of the polyvalent metals, and for salts with other anions.

There are substances (e.g., NH_4CNS , NaI etc.) in solutions of which swelling is markedly stronger than in pure water. In solutions of most substances swelling is less than in water, the diminution being particularly strong in solutions of Na_2SO_4 , LiCl , and BeCl_2 . Such a behaviour has been known since Hofmeister,¹⁰ Pauli,¹¹ Wo. Ostwald,¹² Katz,¹³ and others, published their results on swelling, but in all these cases objections ap-

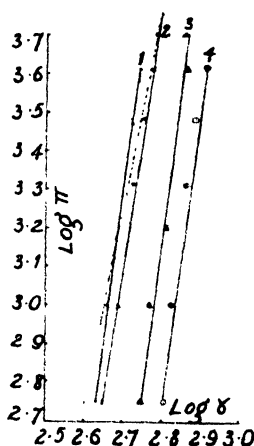
peared justifiable on the grounds that the methods of investigation were not well defined: some were not isothermal or reversible; others were not free from the influence of swelling velocity or peptisation. Our experiments suffered from none of these defects, though the method of comparison was arbitrary in so far as the electrolyte concentration was concerned, and also in comparing the effects at $\gamma = 500$. One could compare the values of Π_0 , but since this is the swelling pressure at a concentration 1, it would mean an extreme extrapolation. A small change in a k -value caused by any experimental error would thus cause a large error in Π_0 . It therefore seemed better to compare values of a swelling pressure for a concentration closer to the region with which the

Swelling in salt solutions.



- 1 TiNO_3 .
- 2 KCl .
- 3 NaCl .
- 4 LiCl .

FIG. 3.



- 1 SrCl_2 .
- 2 CaCl_2 .
- 3 $\text{La}(\text{NO}_3)_3$.
- 4 BeCl_2 .

FIG. 4.

Curve for water shown dotted.

The letter a denotes points reached from a pressure above the final value and b from below.

¹⁰ Hofmeister, *Arch. experim. Pathol. Pharmacol.*, 1891, 28, 210.

¹¹ Pauli, *Pflüg. Arch.*, 1897, 67, 219 and 1898, 71, 1.

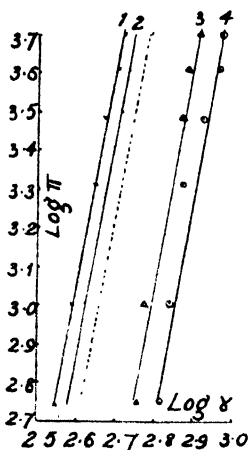
¹² Wo. Ostwald, *ibid.*, 1905, 108, 563, and 1906, 111, 581.

¹³ Katz and Derksen. *Rec. Trav. Chim. Pays-Bas*, 1931, 50, 149; Katz and Muschter, *Biochem. Z.*, 1933, 257, 385 and 397.

measurements had actually been concerned. We took the value of Π for a concentration of $\gamma = 500$, i.e., $\log 2.7$, for here the values could be interpolated or extrapolated only a small amount.

The influence of a change in concentration of the electrolyte has not so far been investigated very thoroughly. In the case of NaCl, full Π/γ

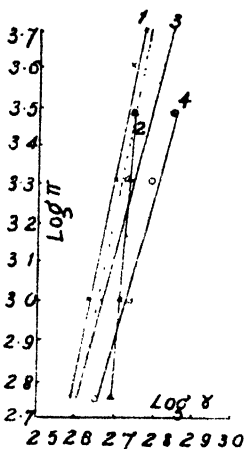
Swelling in salt solutions.



- 1 KIO_3 .
- 2 NaNO_3 .
- 3 NaF .
- 4 Na_2SO_4 .

FIG. 5.

Curve for water shown dotted.



- 1 $\text{N}/2$ NaCl.
- 2 N "
- 3 $\text{N}/5$ "
- 4 $\text{N}/10$ "

FIG. 6.

curves were measured at the additional concentrations of 0.1N , 0.5N , and 1.0N , these readings being supplemented by measurements of the swelling in salt solutions of differing concentrations, but under a fixed swelling pressure. (The p_H values in the three additional cases were respectively 8, 9.5, and 9.5, while the temperatures were 17.5 , 19 , and 17 .)

While in each of the cases just mentioned the linearity of the $\log \Pi / \log \gamma$ curves remained un-

changed, and while the peptisation was small, Fig. 6 shows that the influence of salt concentration was not at all simple. In a range of small concentrations (between 0.1 and 0.5N) swelling shows an initial decrease and then an increase with rising concentration; at higher concentrations it decreases again. Comparison is made difficult, however, by the fact that k rises strongly with increasing concentration, the values being 3.8 , 4.1 , 5.6 , and 14 for 0.1 , 0.2 , 0.5 , and 1.0N solutions. The swelling at a fixed pressure of 1060 gms./sq. cm. is compared in Table II.

Some preliminary results with calcium chloride also gave a rise of k with increasing concentration, but the change in swelling was much smaller. It may be remarked that the measurements of other authors,¹⁴ using quite different methods, have shown that the influence of concentration on the swelling is very complicated.

The solutions of two non-electrolytes were also investigated, namely urea and cane sugar. The urea had a concentration of 0.833 moles/litre, and the cane sugar 0.146 . Both experiments were at 15° , and in both the p_H was 7 . The k -values were respectively 6.0 and 9.5 . In each case

TABLE II.—CHANGE OF GEL CONCENTRATION FOR A GIVEN SWELLING PRESSURE WITH THE CONCENTRATION c OF THE SODIUM CHLORIDE SOLUTION.

c (moles/litre).	γ (gms. isinglass/ 1000 c.c. ising- glass + liquid).
0.00	410
0.06	490
0.08	535
0.10	505
0.20	448
0.25	415
0.50	441
1.00	512
2.00	516

¹⁴ Cf. for instance Wo. Ostwald.¹⁸

the equation held, and the results agree with older results in that cane sugar caused a marked decrease in swelling.¹⁵ The solution of urea was not very different in effect from pure water (cf. Fig. 7).

Now, as isinglass is very similar to gelatin it is probable that it is not simple in its chemical constitution. Northrop and Kunitz¹⁶ fractionated gelatin by a suitable treatment of the aqueous solution with alcohol and at a low temperature (0° C.). They obtained two fractions, the more soluble one having a higher osmotic pressure and a smaller viscosity than the other. An attempt was made to repeat their method with isinglass, and a certain separation was achieved. The two fractions obtained both appeared to be proteins, though their properties were remarkably different. The soluble fraction, which was present in large excess, had a slight yellow colour. It had a strong swelling power, and dissolved with great ease in warm water. These solutions did not gel on cooling unless the concentration was distinctly larger than with the original material. The insoluble fraction had quite the opposite properties. It was a grey powder, only soluble in water with difficulty. Further, when the solution was cooled the result was not a gel, for the material separated in flocks. It was not, therefore, possible to measure the swelling pressure of the latter fraction by our method. This could only be done with the more soluble fraction. It was compared with the original isinglass in a 0.2*N* sodium chloride¹⁷ solution.

Table III. shows that the more soluble fraction has a higher swelling pressure than the original isinglass. This appears to agree with the results of Northrop and Kunitz that their soluble fraction of gelatin had a higher osmotic pressure.

4. These experiments show that the relation between swelling pressure

TABLE III.—COMPARISON OF SWELLING PRESSURE OF ISINGLASS WITH THAT OF ITS MORE SOLUBLE FRACTION (IN 0.2*N* SODIUM CHLORIDE).

Normal Isinglass p_H 8.3, 18.5° C. Slight peptisation.		Soluble Fraction p_H 8.0, 14.5° C. Strong peptisation.	
γ .	II .	γ .	II .
402	560	368	560
455	1060	377	1060
543	2080	456	2060
658	4060	481	4060
690	5050		

and gel concentration given by the equation holds very generally for aqueous solutions. The equation is only empirical, but the range it covers is fairly broad.¹⁸ The impression which might be gained from the experiments mentioned above¹ that the exponent k varies very little with the nature of the gel and of the liquid—being about 3—was not confirmed; k may attain very much higher values—up to 8 or more—in aqueous solutions of high concentration of

the dissolved substance and with electrolytes with polyvalent ions.

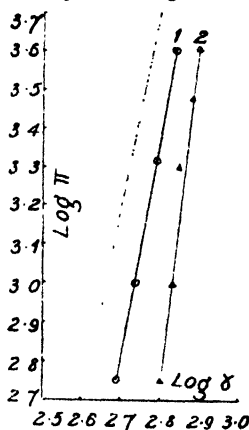
¹⁵ Cf. Hofmeister.¹⁰

¹⁶ Northrop and Kunitz. *J. Gen. Physiol.*, 1927, 10, 167.

¹⁷ The experiments were done in a sodium chloride solution because they are not so well reproducible in pure water.

¹⁸ According to v. Terzaghi³ the equation holds for gelatin in pure water up to a swelling pressure of 52,000 gms./sq. cm.

Swelling in solutions of organic compounds.



- 1 Urea.
- 2 Cane sugar.

FIG. 7.

Curve for water shown dotted.

As mentioned already our experiments concerning reversible and isothermal swelling phenomena agree fully with previous measurements done with less well-defined methods on gels of gelatin, starch, etc.¹⁰⁻¹³

The results show that salts may change the swelling pressure strongly independent of change of p_H . One example may prove this assertion: in a 0.2*N* sodium sulphate solution the p_H of the swollen gel was 8.5. If swelling pressure depended only on the p_H , according to Fig. 2, one would have expected an increased swelling: in water (of a $p_H = 6.0$) a swelling pressure of 3060 gm. sq. cm. would correspond to a gel concentration of 612, whereas for a $p_H = 8.5$ one would have, corresponding to an increased swelling, the smaller value of 520. But in the sodium sulphate solution the gel concentration actually corresponding to this swelling pressure was higher, 865; swelling had decreased.

This behaviour agrees with an assumption, now very generally favoured,¹⁹ that swelling is a complex phenomenon and cannot be explained on the ground of only one physico-chemical process. Most likely, changes in swelling due to a change of p_H have to be distinguished from the changes caused by neutral electrolytes and non-electrolytes. The former phenomenon is frequently explained as a Donnan effect.²⁰ Others²¹ prefer to correlate this influence of p_H upon swelling with a change in the electrical charge of the gel micellae. It seems difficult if not impossible, to correlate the influence of neutral salts with a Donnan effect, because, as was discussed in the example of sodium sulphate, it does not depend on the change of p_H which is observed.

The influence of the ions is obviously related to their position in the lyotropic or Hofmeister's series²² $\text{Li} < \text{Na} < \text{K}$ and $\text{SO}_4 < \text{F} < \text{Cl} < \text{NO}_3 < \text{I} < \text{CNS}$. All facts known so far seem to prove that the order of the ions in these series has to do with the order of their hydration.²³ The ions might influence the swelling by changing the amount of water bound to the gel micelles. This action would depend strongly upon the way in which the ions are distributed in the gel; whether they are bound to the micellae or are in the intermicellar liquid.²⁴ Swelling would be favoured if markedly hydrated ions are adsorbed strongly by the micellae. According to Katz²⁵ this is why the thiocyanate ion and other ions and molecules of similar structure, favour swelling so definitely: they are hydropolar substances containing a hydrophobic and a hydrophilic group; the hydrophobic group is advantageous as to adsorption in an aqueous medium, the hydrophilic one is the cause of the hydration. On the other hand, if the ion is negatively adsorbed (*i.e.*, if it prefers to remain in the aqueous medium) swelling may decrease, so long as the strongly hydrated ion can rob the micelles of their water molecules. It is actually known that sulphates,

¹⁹ For instance Jordan Lloyd and Pleass⁴; Jordan Lloyd and Marriott, *Trans. Faraday Soc.*, 1936, **32**, 932; Kuntzel, *Biochem. Z.*, 1929, **209**, 326. Pauli and Valké, *Electrochemie d. Kolloid.*, 1st edit., p. 428 *et seq.*, 1929.

²⁰ Procter, *J. C. S.*, 1914, **105**, 313. Procter and J. A. Wilson, *ibid.*, 1916, **109**, 307. J. A. Wilson in Bogue, *The Theory and Application of Colloidal Behaviour*, 1924, I, 1.

²¹ Kuntzel.¹⁹

²² Cf. for instance also Jordan Lloyd and Marriot, *loc. cit.*¹⁹

²³ For instance, Remy, *Fort. Chemie, Physik u. physik Chemie*, 1927, **19**, 73.

²⁴ Katz and Muschter.¹³ Cf. also Freundlich, *Kapillarchemie*, 1 edit., 1909, pp. 513-14.

²⁵ Katz and Muschter¹³ Cf. also Katz, Muschter and Weidinger, *Biochem. Z.*, 1933, **259**, 76; **261**, 15, 47, 433; **262**, 355.; **263**, 323; Katz and Weidinger, *ibid.*, 1933, **259**, 191; **263**, 421; 1934, **271**, 54.

for instance K_2SO_4 , are adsorbed negatively by gelatin;²⁶ the same holds for sugars with tanned gelatin, ovalbumen, etc., as adsorbants.²⁷

There does not appear to be a correlation between the influence of salts on swelling and their peptising action; sodium thiocyanate and iodide both cause an increase of swelling, but while the former favours peptisation, the latter does not do so.²⁸

The conception of bound water is, perhaps, still open to objection. But it is a fact that a certain amount of water in concentrated gelatin gels does not turn to ice even at very low temperatures²⁹ and that about the same amount is unable to hydrate blue $CoCl_2$ in a gelatin gel.³⁰ This seems to show indirectly that in concentrated gels, at least, a part of the water is bound very strongly to the micelles and may compete with the water bound to the ions or molecules of dissolved substance.

Summary.

1. The swelling pressure of isinglass in water and aqueous solutions of a number of electrolytes and a few non-electrolytes (urea and cane sugar) has been determined at room temperature with a device similar to that of Posnjak. This could be done because isinglass is peptised in these solutions much less than gelatin.

2. Swelling is reversible. The equation correlating swelling pressure Π and concentration of the gel γ (in grams of isinglass per 1000 c.c. isinglass + liquid) is

$$\Pi = \Pi_0 \gamma^k$$

Π_0 and k being constants.

3. The swelling of isinglass is on the whole similar to that of gelatin, both as to the absolute amount and as to the value of k (4.7 for isinglass and 3 for gelatin). For isinglass in many other aqueous solutions, especially at higher concentrations and with polyvalent ions, k may attain much higher values (8 or more).

4. The influence of different ions was compared at a salt concentration of 0.2N. In the presence of some electrolytes (NaI , NH_4CNS) swelling is stronger than in water. In that of others (specially Na_2SO_4 , $BeCl_2$, and $La(NO_3)_3$) it is markedly less. These changes do not depend on the small changes of p_H caused by the electrolytes. As to the intensity of their effects the ions may be arranged in Hofmeister's series $Li < Na < K$ and $SO_4 < F < Cl < NO_3 < I < CNS$.

5. The influence of the electrolyte concentration c was investigated thoroughly only in sodium chloride solutions. It was not at all simple; k increases with increasing c , especially at higher salt concentrations.

6. The influence of p_H on the swelling of isinglass was measured in acetate buffer solutions in a range between 2.8 and 9.5 at a constant swelling pressure of 1060 gms./sq. cm. There was a minimum of swelling at about 6.5, close to the isoelectric point of isinglass (about 6). A minimum of swelling near the isoelectric point has also been found in other cases.

²⁶ Dumanski, *Z. physik. Chem.*, 1907, **60**, 559. Cf. also the well-known experiment with pig's bladder and a very concentrated sodium chloride solution performed by Ludwig (*Pogg. Ann.*, 1849, **78**, 320).

²⁷ R. O. Herzog, *Z. physiol. Chem.*, 1908, **57**, 315. Herzog and Adler, *Kolloid. Z.*, 1908, **2**, II. Supplem., p. iii. Berczeller, *Biochem. Z.*, 1918, **90**, 290.

²⁸ Hence we do not agree with Holwerda, *Biochem. Z.*, 1935, **282**, 340, that increased swelling always leads to increased peptisation.

²⁹ Moran, *Proc. Roy. Soc., A*, 1926, **112**, 30.

³⁰ Hatschek, *Trans. Faraday Soc.*, 1936, **32**, 787.

7. The swelling of isinglass decreases markedly in the presence of sugar; urea has a weaker influence in the same sense.

8. The gold number of isinglass was 0.0055, fairly close to the value found for gelatin with the same gold sol (0.01).

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NOTE ON THE RELATIONSHIP BETWEEN ζ POTENTIAL AND STABILITY IN EMULSIONS.

BY CONMAR ROBINSON.

Received 16th June, 1936.

Harkins and his co-workers have carried out work which indicates that the stability of an emulsion increases in general as the emulsifying film changes from an expanded to a condensed film.^{1,2} Thus, if an oil emulsion is formed with sodium oleate, Fischer and Harkins were able to show (by determining the size distribution of the droplets) that at first the droplets increase in size, but eventually reach a stable size distribution. Further, when this stable size distribution is reached they showed, by determining the amount of sodium oleate adsorbed on the droplets, that the interfacial concentration of sodium oleate corresponds to a condensed monomolecular film.

The following theoretical point which gives one reason for the importance of the condensed monomolecular film does not seem to have been previously discussed.

If we consider an oil in water emulsion stabilised by a paraffin chain electrolyte such as sodium oleate, the ions will be symmetrically distributed on the surface of the droplets, with the paraffin tails embedded in the oil and the lyophilic heads turned towards the water. The concentration of ions on the surface, even though it is not enough to give a condensed monomolecular layer, may be enough to give a charge density and resulting ζ potential which would be high enough in the case of a lyophobic sol to prevent the particles from coming into contact with one another. With the liquid particles of an emulsion, however, we suggest there will be a very important difference. As the droplets approach one another, the long chain ions, the negatively charged heads of which repel one another, will be redistributed, the ions slipping round the surface of the droplets until there are comparatively few ions on the opposing faces. Consequently, the ζ potential at that part of the surface of each droplet nearest the approaching droplet will be lowered so much that coalescing will take place.

If, however, there is a condensed monomolecular film on the surface, the ions cannot slip round the droplets and hence we have the optimum conditions for stability. (It would seem probable that a surface concentration very near to that which would give a condensed monomolecular film would be equally efficient provided the ions on the interface were

¹ Harkins and Beeman, *J.A.C.S.*, 1929, **51**, 1674.

² Fischer and Harkins, *J. Physic. Chem.*, 1932, **36**, 98.

sufficiently crowded together to correspond to the steep portions of the force area/curve, *i.e.* where a considerable increase in lateral pressure is necessary to bring about any further decrease in the area occupied by an ion.) Thus while the stability of a lyophobic sol is dependent on the ζ potential of the particles exceeding a certain critical potential X , which will be given by a comparatively low surface concentration A (see Fig. 1), the stability of an emulsion will not be governed by the ζ potential of the isolated particle (curve I), but by the ζ potential on opposing faces of close drops (curve II) which will only reach X at some higher surface concentration B . Only where the surface concentration reaches the value for a condensed monomolecular film will the ζ potential of the isolated particle in the emulsion be the same as that at the opposing faces of near drops.

Hence, when considering the stability of oil emulsions stabilised by paraffin chain ions, it is most important to determine the

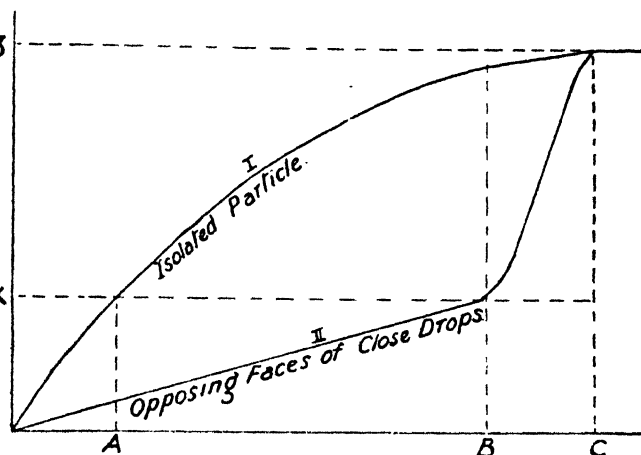


FIG. 1.

concentration of solution which will give a surface concentration which is nearly that corresponding to a condensed monomolecular film. This surface concentration will probably be attained with a solution concentration of paraffin chain electrolyte which gives the maximum lowering of interfacial tension. On the other hand, cataphoretic measurements will be of little interest, as these can only give the ζ potential of the isolated drops.

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ON THE MICROTHERMOCONDUCTIVITY METHOD FOR THE ESTIMATION OF PARA-HYDROGEN AND DEUTERIUM.

BY D. D. ELEY AND JAMES L. TUCK.

Received 18th June, 1936.

The microthermoconductivity apparatus for the estimation of *para*-hydrogen, invented by A. Farkas¹ and extended by A. and L. Farkas² to the estimation of deuterium, has been successfully used by a number

¹ A. Farkas, *Z. physik. Chem., B*, 1933, **22**, 344.

² A. Farkas and L. Farkas, *Proc. Roy. Soc., A*, 1934, **144**, 467.

of workers,³ some of whom mention the practical difficulties involved in the application of this method. A modified version of the apparatus has been published by Wirtz,⁴ who also gives a discussion of the technical points concerned. In connection with an investigation of the exchange reaction between hydrogen and water, an apparatus similar in some points to that of Wirtz, has been independently developed in these laboratories. In view of its importance for this work, and the practical difficulties experienced in its construction, it has been considered desirable to publish a short account.

The Apparatus.

The essential points are shown in Fig. 1. The cell G, of soft glass, contains a loop of platinum strip wire⁵ (0.05 mm. \times 0.005 mm.) 17 cm. long, held taut by a quartz-fibre and silver-soldered at each end to the

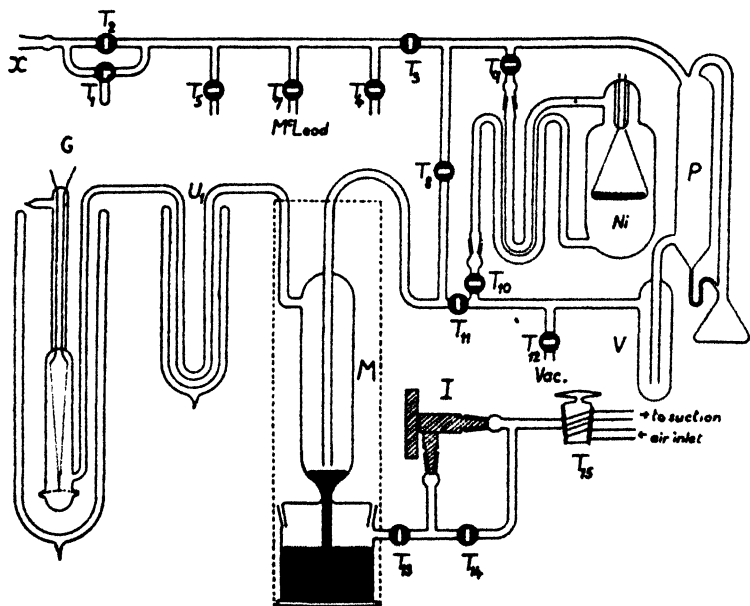


FIG. 1.

sealing-in wire. The leads to the cell are taken through an evacuated stem⁶ (20 cm. long) and the whole gauge is deeply immersed in a bath of liquid air, the level of which is kept constant (a thermocouple junction, not indicated, is used to "detect" the level, and from time to time liquid air is blown in from a siphon). U_1 protects the cell from Hg vapour, tap-grease, and so on. M has a volume of 150 c.c. and serves both as a cut-off, eliminating taps in the vital part of the system, and as a pressure-adjusting device.* An asbestos box, indicated by dotted lines, protects it from

³ E.g. E. Fajans, *Z. physik. Chem.*, B, 1935, **28**, 239; K. Wirtz, *ibid.*, B, 1935, **30**, 289; Reitz and Bonhoeffer, *ibid.*, A, 1935, **172**, 369; Taylor and Diamond, *J. Amer. Chem. Soc.*, 1935, **57**, 1256; F. Patat, *Z. physik. Chem. B*, 1936 **32**, 283.

⁴ K. Wirtz, *Z. physik. Chem.*, B, 1936, **32**, 335.

⁵ Knauer and Stern, *Z. Physik*, 1929, **53**, 766.

⁶ See also Taylor and Diamond.³

* This eliminates the use of a needle-valve. We found needle-valves to have the following disadvantages: (a) they were not really vacuum tight, (b) imperfections in grinding and fluctuations in pumping speed gave an imperfect adjustment of pressure, (c) they gave a separation of the hydrogen isotopes (see ⁴).

draughts; the gauge is very sensitive to pressure alterations consequent on room temperature fluctuations and it is essential that the pressure in the cell should be constant over one minute, which is the time required for a resistance reading. The cell Ni contains the heated nickel wire which is used to bring $p\text{H}_2 \rightleftharpoons n\text{H}_2$ reaction to equilibrium; liquid air traps protect it from tap-grease, etc. Calibration gases are admitted through taps T_3 and T_4 , the unknown mixture at x .

The Measurements.

For the theory of the apparatus, the reader is referred to the papers of Farkas,^{1, 2} whose symbols we use in the following.

Hydrogen is introduced via T_3 and its pressure (as indicated on the galvanometer, with a given current i_1 , and the Wheatstone bridge set at R_1) is lowered by pumping via a "lock," until it is lower than required. The mercury in M is then run up, and by use of the vent, I, the pressure in the gauge can be very accurately adjusted.

The measurements concerned are analyses of $p\text{H}_2$ and HD in mixtures of the two (deuterium < 4 per cent.). Because of drifts in resistance value, it is found necessary to measure $n\text{H}_2$ with every experimental determination, and to measure a calibration mixture of $p\text{H}_2$ and HD every day. Measurements are made in the order $n\text{H}_2 = \Delta$ ohms; $p\text{H}_2 + \text{HD} = \Delta + (a + b)$; the gas is now brought to equilibrium by circulation over the red-hot nickel wire, and introduced into the cell, $n\text{H}_2 + \text{HD} = \Delta + a$; $n\text{H}_2 = \Delta$. Then $[p\text{H}_2] \sim b$, $[\text{HD}] \sim a$. 3.2 per cent. D gas gives $a = 0.45 \Omega$ on our apparatus, the value varying from day to day by 0.01 Ω , with maximum fluctuations of $\pm 0.03 \Omega$. Δ has been observed to decrease 0.3 Ω in a day, but after some days' working it becomes fairly constant. The resistance values a and b are reproducible to $\pm 0.01 \Omega$ or ± 0.1 per cent. D. The diurnal decrease of Δ may be due to alteration in accommodation coefficient, or solution of hydrogen in the wire with subsequent diminution of the temperature coefficient of resistance.³

A number of points in connection with the apparatus have been observed:—

1. Increase of temperature of the liquid air round the cell decreases the resistance shifts, particularly that due to HD.
2. Each time the gauge is first adjusted an "adsorption effect" occurs. On making the necessary current adjustments and resistance measurements, $i_1(R_1)$, $i_2(R_2)$, then back to $i_1(R_3)$, it is found that $R_3 < R_1$, in fact, $R_1 - R_3$ is of the order of 0.05 Ω , indicating a slight increase of pressure in the gauge. The pressure is readjusted and measurements made until $R_1 = R_3$ within 0.005 Ω .
3. With the "untreated" wire, $p\text{H}_2$ conversion has been observed in the cell, giving a very quick drift of resistance value down to the deuterium value ($\Delta + a$), where it remains constant. The conversion does not go at T_1 , but only at the higher T_2' and so goes through the "high-temperature mechanism." It was stopped by poisoning the wire with hydrogen in the treatment outlined below. (The poisoning effect of hydrogen on this type of reaction is well known.^{4, 5})
4. Finally, a treatment was developed for putting the cell into working condition after accidental admission of air, etc. The objects are (a) to clean the wire, (b) to give an adsorbed layer of hydrogen stable at the working pressure (0.05 mm. Hg) and the upper temperature T_2' (about 0° C.), (c) to poison the wire to the $p\text{H}_2$ conversion.

¹ R. Suhrmann, *Z. Physik*, 1923, 19, 1; K. Hermann, *Ann. Physik*, 1925, 77, 503.

² Emmet and Harkness, *J. Amer. Chem. Soc.*, 1935, 57, 1631 (Fe, Pt).

³ Burstein and Kashtanow, *Trans. Faraday Soc.*, 1936, 32, 823, (charcoal).

The cell is pumped for about six hours at 150° C., "overheating" the wire (resistance at 0° C. equals 100 Ω) with 10 mA. Liquid air is round U₁. The wire is then glowed red for thirty seconds, and then both wire and cell are reduced slowly in temperature over five hours. 10⁻¹ mm. of H₂ are left in the cell overnight; the liquid air bath is then placed round the cell and the H₂ pumped away. A number of actual "measurements" serve to bring about the fine adjustment of the sorbed quantity of hydrogen, upon which the stable working of the apparatus appears to depend.

In general, five minutes are spent over a measurement (i.e. about twenty minutes for a complete analysis of *p*H, and HD, including the time required for pumping). The minimum quantity of gas that can be handled with our apparatus, which has a large dead space, is about 0.05 c.c. at N.T.P. It should be possible to reduce this to 0.01 c.c., by using a circulating pump with a smaller dead space and cutting down the volume of the cut-off and the tubing.

The authors wish to express their best thanks to Professor M. Polanyi for invaluable help and advice.

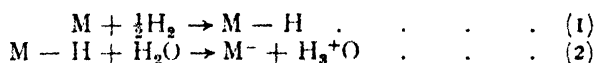
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THE PLATINUM ELECTRODE AS A CATALYST FOR THE ACTIVATION OF HYDROGEN.

BY M. CALVIN.

Received 24th June, 1936.

It has long been known that metals catalyse the establishment of the equilibrium between H₂ molecules and H⁺ ions in solution, but the precise mechanism has not yet been completely elucidated. The essential series of reactions usually considered is



Upon the assumption that (2) or its reverse is the rate determining step in the deposition of hydrogen, Erdey-Gruz and Volmer¹ and Frumkin² have given a derivation of the empirically found relation

$$\epsilon = a + b \log i \quad (3)$$

between current *i* and cathodic overvoltage ϵ (high) at a hydrogen electrode. Horiuti and Polanyi³ have recently extended this conception and given a more detailed account of the mechanism of the reaction with some plausible reason for the value of the constant *b*. Upon the basis of an analysis of the current-voltage relation for small polarisations, which does not conform to equation (3) Hammett⁴ came to the conclusion that the speeds of processes (1) and (2) were both of the same order of magnitude, and that small variations in the condition of the electrode

¹ Erdey-Gruz and Volmer, *Z. physik. Chem.*, A, 1930, 180, 203.

² Frumkin, *Z. physik. Chem.*, A, 1933, 164, 121.

³ Horiuti and Polanyi, *Acta Physicochimica U.S.S.R.*, 1935, 2, 520.

⁴ Hammett, *Trans. Faraday Soc.*, 1933, 29, 770.

(polarisation, surface, etc.) might make one or the other predominant. The same conclusion has been arrived at by Knorr and Schwartz.⁶

In all of these theories there are two opposing currents, that of oxidation and that of reduction, which are balanced at the potential of the reversible hydrogen electrode. Should this be the case it is reasonable to assume, with Horiuti and Polanyi, that the exchange reaction between deuterium and water



which has been shown to be catalysed by platinum black⁶ should go through such a series of steps and should provide a measure of the two currents flowing at zero overvoltage. If (2) is the limiting process the rate of exchange should be affected by the polarisation of the electrode at which it is measured. The following contains a report upon some exploratory experiments done to measure this effect and also the effect of polarisation upon the para-ortho-hydrogen conversion.

Experimental.

The apparatus used is shown diagrammatically in Fig. 1. It consisted essentially of a

reaction vessel V, containing the catalyst electrode E, a polarising anode A, a hydrogen reference electrode H, and a tube T leading to the saturated calomel electrode C. This was connected to a circulating pump and the high vacuum pumps so that the system could be well evacuated and a given sample of $\text{H}_2 - \text{D}_2$ gas circulated through the cell for long periods of time. M is a manometer, J a water jacket for condensing water vapour from

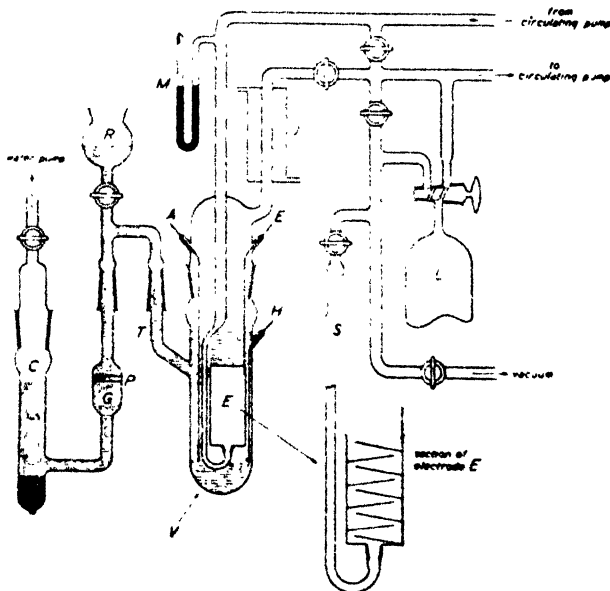


FIG. 1.

the outward flowing gas, and at S a sample bulb could be attached for withdrawing a quantity of the hydrogen to be analysed for its deuterium content. This analysis was made by means of a quartz-fibre gas density micro-balance, constructed after the design of Whytlaw-Gray, Patterson and Cawood,⁷ and could easily be carried out to within 0.1 per cent.

⁶ Knorr and Schwartz, *Z. physik. Chem., A*, 1930, **176**, 161; *Z. Electrochem.*, 1934, **40**, 38.

⁷ Horiuti and Polanyi, *Nature*, 1933, **132**, 931; 1934, **133**, 142.

⁸ Whytlaw-Gray, Patterson and Cawood, *Proc. Roy. Soc.*, 1931-32, **134**, 7. The author is indebted to Dr. Cawood for personal advice concerning the construction of the balance.

The polarising current was drawn from a 110 volt dry battery through a variable high resistance, so that the polarisation in the cell did not alter the current density, once set. The potential measurements were made on a Cambridge potentiometer capable of measuring 0.01 millivolt.

Since the pressure in the cell was always less than atmospheric it was necessary to make the connection to the calomel cell through a sintered glass plate P, backed by a fairly hard agar gel G made in saturated KCl. This was found to give satisfactory electrical connection and would hold the atmosphere against 17 mm. (vapour pressure of water) with only an extremely slow leak of about 5 c.c. of solution in a week. This could be completely eliminated by reducing the air pressure in the calomel cell to something only a few mm. higher than that existing in the reaction vessel V. The whole reaction vessel V, could be immersed in a dewar flask containing ice water. The total volume of reaction vessel and circulating system was 800 c.c.

All the metal electrodes were made of platinum, the anode A and the hydrogen electrode H being 0.5 mm. wire. The electrode E is shown in section. It is a square tube 5 cm. long and 2 cm., on a side, containing nine baffle plates arranged as shown, made of plate 0.05 mm. thick. The total area both inside and out is 150 cm.² Thus the gas in passing up through the baffles must make intimate contact with the metal, and since between each stroke of the circulating pump the electrode fills with solution which must be pushed out again at the next stroke, the solution is also well stirred by the circulating gas.

All three electrodes were platinised in the usual manner from a 3 per cent. solution of platinum chloride containing 0.025 per cent. of lead acetate. The electrode E was never made anodic in the course of this process, H being used to platinise A. During the course of the experiments the electrode remained jet black in colour except after it had been made anodic for a considerable period after which it became grey.

The hydrogen used was about 99 per cent. D, made by electrolysis the corresponding heavy water in a KOH solution. It was purified by passage through a palladium thimble.

Procedure. After the electrodes had been platinised and cleaned of traces of chloride by cathodic discharge of hydrogen and washing in distilled water, the cell was assembled and evacuated until the pressure of residual gas was less than 10^{-5} mm. The solution was then admitted from the reservoir R until it covered the electrode E. This solution contains dissolved air and the pumping is again continued until the residual gas pressure falls to less than 10^{-4} mm. The system is allowed to stand evacuated for 24 hours and any gases which may have come out of solution during that time are again pumped off. A sample of thimble ordinary hydrogen is then admitted through the tap S and circulated through the cell for a few minutes to saturate the solution with hydrogen and then the process of evacuation is repeated. After this deuterium is admitted to the desired pressure, 200-300 mm., circulated for a few minutes and a sample for analysis taken in a liter bulb at S. About 200 c.c. of gas at 300 mm. pressure are required for analysis but this gas is returned to the system with only a small loss, by means of the gas transfer vessel, L, so that after each sample is taken and returned the total pressure of the system has fallen only by 5 to 8 mm. In the case of the pH_2 , conversion only very small samples were required since the analysis was made by means of the micro-thermal conductivity method of Farkas, and many samples could be completely removed without appreciably altering the pressure.*

Results. In the first experiments done in water the polarisation of the electrode was not measured because of the low conductivity of the solution and the consequent high ohmic drop in the solution between the standard electrode and the catalysing electrode. The exchange reaction

* Thanks are due to Mr. D. D. Eley for making these measurements.

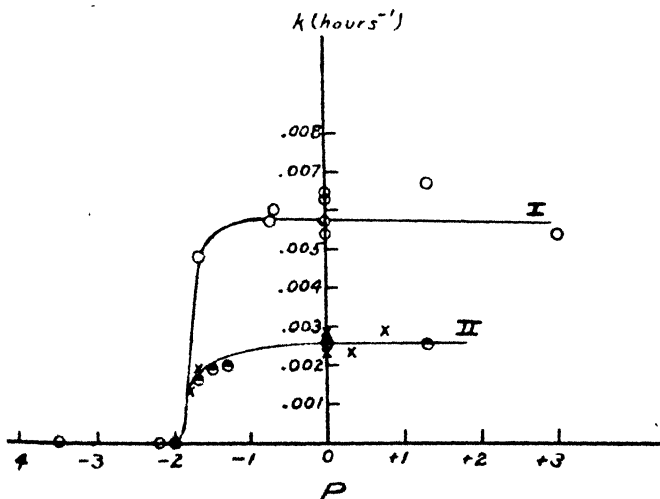
velocity was measured as a function of the potential difference maintained between the anode A and the electrode F. The data so obtained at 20° C. and 0° C., are given in Table I. and plotted in Fig. 2, the points for water being represented by circles. In the Table, P is the polarizing potential maintained between A and F and p is the pressure of the gas in the system. The data is tabulated in the order in which they were obtained showing that the changes there apparent are quite reversible. The variation in the unimolecular velocity constant $k = 1/t$ in C_0/C_t to be expected from the variation in pressure appearing here is within the experimental error ^{9, 10} of k .

In Table II. are given the results obtained on 0.01 N H₂SO₄, the plate having been replatinised between these measurements and the preceding ones.

ϕ_0 and ϕ are the potentials of the unpolarised and polarised plate respectively against the saturated calomel electrode; $\Delta\phi$ will then be the over-voltage or polarisation of the

TABLE I.

p mm.	Original PerCent. D.	Time (hrs.).	Final PerCent. D.	Polarisa- tion P.	k hrs. ⁻¹ .
<i>In water at 20° C.</i>					
189	89	17.2	79.4	0	0.0065
181	79.4	21.6	69.2	0	0.0064
304	92.4	12	86.1	-0.7	0.0060
295	86.1	9.67	81.7	0	0.0057
270	81.7	35	68.2	0	0.0052
265	68.2	6	68.2	-3.5	0
257	68.2	11	64.2	3.0	0.0054
251	64.2	8.5	60.2	0	0.0073
245	60.2	12	60.2	-2.2	0
243	60.2	7.5	57.2	1.3	0.0067
238	57.2	11.5	53.6	-0.75	0.0057
234	53.6	8.17	51.4	-1.7	0.0048
225	51.4	12.5	51.4	-2.0	0
220	51.4	20.6	45.6	0	0.0057
<i>In water at 0° C.</i>					
350	90.3	18.25	86.2	0	0.0026
336	86.2	22	82.4	-1.3	0.0020
330	82.4	21	78.2	1.3	0.0025
323	78.2	23.5	74.5	1.5	0.0019
316	74.5	25.5	71.4	-1.7	0.0016



I. At 20° C. II. At 0° C.

FIG. 2.

respect to the reversible hydrogen electrode in that particular solution. The current, i , is that required to maintain the corresponding polarisation, and it flows between the anode A and the electrode F. The data in this table are also presented in the order in which they were taken. These data are again plotted in Fig. 2 and

⁹ Horiuti and Polanyi, *Proc. Manc. Lit. Phil. Soc.* 1934, 48, 47.

¹⁰ Polanyi and Eley, *This No.*, p. 1388.

TABLE II.

p (mm.).	Original Per Cent. D.	Time (hrs.).	Final Per Cent. D.	ϕ_0 .	ϕ .	$\Delta\phi$.	i (mils.).	k (hrs. ⁻¹).
In 0.01 N H ₂ SO ₄ at 0° C.								
374	99.8	23	93.8	-0.34	-0.34	0	0	0.00269
366	93.8	21	90.1	-0.37	-0.38	-0.01	0.5	0.0186
360	90.1	20	85.8	-0.37	-0.37	0	0	0.0244
353	85.8	24	83.1	-0.325	-0.35	-0.025	0.7	0.0133
347	83.1	42	74.7	-0.35	-0.35	0	0	0.0253
337	74.7	21.8	71.3	-0.345	-0.230	0.115	2.0	0.0230
332	71.3	21.8	66.8	-0.34	-0.34	0	0	0.0288
327	66.8	24	62.3	-0.348	-0.06	0.408	3.25	0.0288
320	62.3	21.5	58.3	-0.36	-0.36	0	0	0.0249
317	58.3	24.3	57.2	-0.343	0.47	.81	5.0	0.0076
312	57.2	41	55.1	-0.33	-0.33	0	0	0.0085

the points are represented by x. The cathodic polarisation was not carried any further because of the commencement of gas evolution. The temperature variation of k obtained from measurements at 20° at 0° C., and back again to 20° C., gives an activation energy of 8100 calories for the exchange reaction.

A series of measurements using the electrode H as a reference electrode was also carried out, but it was found that the potential of H was very greatly influenced by the condition of the electrode F, and hence the

results, although qualitatively the same as the other experiments cannot be quantitatively compared with them.

A series of experiments to determine the effect of potential upon the rate of pH_2 conversion was run in N H₂SO₄. Gas containing about 3 per cent. D and about 20 per cent. excess pH_2 over the equilibrium concentration was introduced into the system, and then small samples withdrawn at the desired intervals to be measured for their HD and pH_2 content simultaneously.* The results, though as yet only qualitative, indicate that the pH_2 conversion is accelerated under those conditions which retard the exchange reaction.

In order to establish the relationship between the electrode

used here and those used by other workers the change of potential with quantity of electricity passed was determined, in addition to the ordinary current-polarisation measurements. The potential-coulomb curves were taken between the small platinised electrodes A and H in 0.01 N H₂SO₄ saturated with hydrogen at 277 mm. pressure. Starting with H in the condition of the reversible hydrogen electrode it was made anodic and a constant current allowed to pass. The change of potential as measured against the saturated calomel electrode is plotted as a function of time and

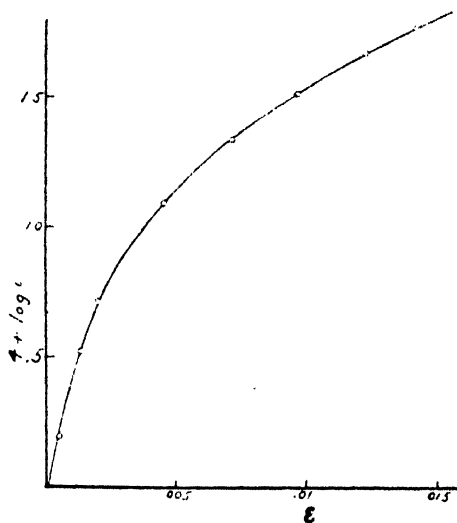


FIG. 3.

the result is in agreement with that of Slygin and Frumkin¹¹ with the depolarising action of the dissolved H_2 taken into account. The curves obtained by plotting $\log i$ against cathodic polarisation were similar to those obtained by Hammett⁴ and by Knorr and Schwartz.⁵ A typical result is shown in Fig. 3.

Discussion.

One fact, immediately evident from these data, is that a comparatively small cathodic polarisation has the effect of greatly reducing the reaction velocity of the exchange reaction and that rather large anodic polarisations up to a certain point have no effect upon this reaction velocity. These data are as yet insufficient to warrant an attempt at a full quantitative interpretation. We will be concerned here with pointing out the restrictions that must be imposed on any theoretical explanation of these results.

Anodic polarisation has no effect upon the velocity constant below about 0.7 volt positive to the reversible hydrogen potential. This result has been recently reported for a Ni electrode by Horiuti and Okamoto.¹² If the plate is kept at some potential higher than this for a time long enough to measure the exchange velocity (10-20 hours) the velocity constant is reduced, irreversibly, to practically zero if the plate is sufficiently positive, and even prolonged cathodic discharge of hydrogen will not reactivate the surface. It is interesting to note that this critical potential of about 0.7 volt corresponds to a point of inflection in the potential-coulomb curves described by Slygin and Frumkin,¹¹ and also observed on this particular electrode. It is reasonable to believe that at this point the attack of the metal atoms of the electrode by the discharged anions commences and thus the surface is irreversibly changed as far as its catalytic activity is concerned.¹³

Before any predictions concerning the effect of potential on the exchange velocity can be made, it should be noted that the passage of a current to or from the electrode must increase the rate of exchange by the corresponding amount. Since no oxygen is evolved (it would appear in the gas and manifest itself in the gas density measurements immediately), it must be reduced at the anode by dissolved hydrogen as fast as it arrives and hence deuterium would disappear from the gas in proportion to the current passed, while exactly the same amount of hydrogen would appear at the cathode, which is already saturated with hydrogen. The relevance of this effect can be estimated from a comparison of the velocity constant on the unpolarised plate with the current passed for polarisation. The velocity constant of the exchange reaction can be expressed as a pair of equal oppositely directed currents and the value of k_0 at 20° C., 0.0062, gives an equilibrium current for the plate used of 4.7×10^{-3} amps., taking 800 c.c. for the volume of the gas at 300 mm. pressure. At 0° C. this would be reduced to 1.9×10^{-3} amps. These are to be compared with the currents of the order of 10^{-3} amps. which are required to maintain cathodic overvoltages around 0.01 volt and currents up to 5×10^{-3} amps. for the anodic polarization, at this same electrode. It is apparent that in acid solutions the exchange due to electrolysis would be an important part of the total exchange both for cathodic and anodic

¹¹ Slygin and Frumkin, *Acta Physicochimica U.S.S.R.*, 1935, **3**, 791.

¹² Horiuti and Okamoto, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, 1936, **28**, 231.

¹³ Butler and Drever, *Trans. Faraday Soc.*, 1936, **32**, 427; Previous work cited.

polarisation. This excess exchange was not observed even when the current passed corresponded to more than 50 per cent. of the total amount of hydrogen in the system. In the case of pure water as the electrolyte, the electrolysis current was always negligibly small and hence it was possible in this case to get a complete cessation of the exchange reaction as far as could be measured by the means employed.

It is evident that (2), ionization, cannot be rate determining, since in that case the velocity constant should vary with polarisation ϵ according to (3),

$$\ln k_{\epsilon} = \ln k_0 + \frac{\alpha \epsilon F}{RT} \quad . \quad . \quad . \quad . \quad (5)$$

neglecting the smaller of the two balanced equilibrium currents the difference between which constitutes the electrolysis current.* Hence anodic polarisation should increase the rate of the exchange. If anything, the anodic polarisation actually reduces the catalytic exchange.

It may be suggested that the inability of anodic polarisation to accelerate the reaction according to (5) might be due to the limiting processes of solution or diffusion of molecular hydrogen, both of which would be unaffected by polarisation. These possibilities are rejected since the temperature coefficient of the reaction velocity is too large for such limiting processes, and moreover it seems that the para hydrogen conversion can be made to go as much as ten times faster than the exchange reaction by simply applying a small cathodic overvoltage.

The retarding effect of cathodic polarisation eliminates the possibility that (1), atomisation, be rate determining provided the atoms and molecules are in such a condition on the metal surface as to be unaffected by polarisation.

It is important to note that the form of equation (5) remains the same, if the exchange reaction velocity is assumed to be effectively limited by any single process, the activation energy of which is the only quantity effected by polarisation. We therefore turn to considerations in which the effect of two consecutive phases is taken into account.

Upon the basis of work on the current-overvoltage relation it has already been proposed by Hammett⁴ that both (1) and (2) are important in limiting the rate of hydrogen deposition. If the activation energies of the two successive processes are about equal and are not affected by polarisation in the same way it may be possible to reconcile our results with such a mechanism. In order that polarisation may have an effect on the activation energy of (1), it is necessary that the structure M—H or M—H₂ be electrically asymmetrical, i.e. polar. From a consideration of the effects of adsorbed gases and vapours upon the thermionic and photoelectric properties of metals it has been quite definitely shown that the surface electric fields of metals distort the adsorbed atoms or molecules with the resultant formation of dipoles.^{14, 15} Suhrmann and Csech have reported that adsorbed hydrogen atoms lower the work function of such metals as Pt, Au, Ag, and hence the dipoles should be oriented with their positive ends away from the metal surface.¹⁶ The

* Actually these currents cannot be neglected in the polarisation ranges under discussion, but the simplified equation is used since this abbreviates the arguments without effecting its result.

¹⁴ J. H. De Boer, *Electron Emission and Adsorption Phenomena*, Cambridge, 1935.

¹⁵ De Boer, and Veenemans, *Physica*, 1935, 2, 915.

¹⁶ Suhrmann and Csech, *Z. physik. Chem., B.*, 1935, 28, 215.

opposite conclusion as to the orientation of the dipoles of adsorbed hydrogen on tungsten has been reported by Roberts¹⁷ upon the basis of experiments indicating a decrease in the heat of adsorption of hydrogen on tungsten with increasing fraction of the surface covered. For metals in contact with hydrogen and acid solutions Bowden¹⁸ has indicated that the dipoles will have their positive ends away from the metal surface while Slygin and Frumkin¹¹ propose the reverse. Since both Roberts, and Slygin and Frumkin base their conclusions upon observations of the work of removal of the first monatomic layer of hydrogen on the metal surface, while Bowden, and Suhrmann and Csech were certainly working with more completely saturated surfaces it may well be, as De Boer¹⁴ has proposed for adsorbed alkali atoms, that the primarily adsorbed layer of dipoles is oppositely oriented from the successive ones. In any case, whichever way the dipoles may be oriented, a change in the electric field in which they are situated will affect the activation energy of their combination.

Another possibility is that other factors besides the activation energy are affected by polarisation. Upon the assumption that a single reaction dominates in limiting the reaction velocity the general relation for the variation in reaction velocity constant with any parameter (in this case polarisation P), as given by Evans and Polanyi,¹⁹ can be introduced. It is given by

$$\frac{\partial \ln k}{\partial P} = \frac{\beta_1 - \beta_r}{RT} \quad (6)$$

where β_1 is the derivative of the free energy of the initial state with respect to the parameter P (polarisation) and β_r is the same quantity for the transition state. Thus in general β is given by

$$\beta = \frac{\partial(H - TS)}{\partial P} \quad (7)$$

where H , T , and S , have their usual thermodynamic significance. If the entropy term is independent of polarisation equation (5) is obtained if $H_r - H_1$ is taken as the activation energy of the reaction. But as has already been indicated the structures $M-H$ and $M-H_2$ are in all probability polar and hence the entropy of these states will not be independent of polarisation and an effect of polarisation upon terms other than the activation energy must result.

These possibilities are being fully investigated in these laboratories and a comprehensive discussion will be withheld until these results are available.

The author wishes to express his great indebtedness to Professor M. Polanyi for suggesting these experiments, for many discussions and his constant interest in this work, and for the opportunity to work in these laboratories.

Summary.

1. The exchange reaction $D_2 + H_2O \rightarrow HD + HDO$ catalysed by a platinized platinum electrode has been investigated in neutral and acid solution.

¹⁷ J. K. Roberts, *Proc. Roy. Soc.*, 1935, **152**, 459.

¹⁸ Evans and Polanyi, *Tr. Far. Soc.*, p. 1333.

¹⁹ Bowden, *Proc. Roy. Soc.*, 1929-30, **126**, 107.

2. It has been found that small cathodic polarisations retard the reaction reversibly, while large anodic polarisations up to about .7 volt do not increase the reaction velocity. At higher anodic polarisation the reaction is irreversibly inhibited.

3. Some theoretical implications of these results are discussed, and it is shown that no unmodified existing theory can account for them.

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ACTIVATION OF HYDROGEN BY PHTHALOCYANINE AND COPPER PHTHALOCYANINE.

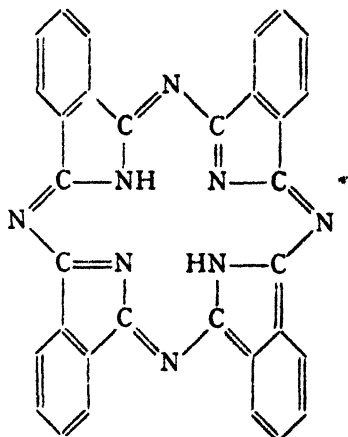
PART I.

BY M. CALVIN, E. G. COCKBAIN AND M. POLANYI.

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The experiments reported in this paper were undertaken in the hope of throwing some light on the mechanism by which enzymes activate hydrogen. While the activation of hydrogen by metal catalysts and the similar action of metal oxides can, to some extent, be accounted for by the formation of surface hydrides, it is as yet completely unknown how an organic compound, such as the enzyme must be, can act as a hydrogenase.

The observations described below, that crystals of phthalocyanine and of copper phthalocyanine can activate molecular hydrogen, might indicate a line of approach to this problem. We seem to have here a pure organic body activating hydrogen, and we have reason to hope that the mechanism of this action will not be difficult to elucidate. It is significant that phthalocyanine contains a central ring very similar to that of porphin, which is the structural nucleus of chlorophyll and hæmin, as well as of various enzymes related to hæmin playing a part in biological oxidation. The structure of phthalocyanine as proved by Linstead¹ is



¹ R. P. Linstead, *J.C.S.*, 1934, 1016.

The existence of a long chain of conjugated double bonds in phthalocyanine also suggests an analogy to the numerous biologically active substances containing such chains. The questions arising from such considerations are being considered in a theoretical communication by Mr. M. G. Evans and one of the authors. In this and the following paper we shall describe only our first observations on the action of phthalocyanine and some parallel experiments with copper phthalocyanine.

Materials.

Our samples of phthalocyanine and of copper phthalocyanine were both obtained by the courtesy of the Imperial Chemical Industries Ltd.; the compounds were prepared and purified by Dr. R. P. Linstead as described by him. We are greatly indebted to both Messrs. The Imperial Chemical Industries Ltd., and Dr. Linstead for their help in making this work possible.

The samples were composed of purple prismatic crystals about 0.5 mm. long and 0.3 mm. thick. The shape of these crystals was similar to those described by Robertson² in his X-ray analysis of the phthalocyanines. On distillation in vacuo at 400° C. our samples of phthalocyanine sublimed without leaving a residue. The formation of a trace of a white substance (probably phthalodinitrile) was observed, and occasionally, when the distillation was carried out at higher temperatures, some green non-volatile residue, insoluble in quinoline, was obtained. A microanalysis of 50 mg. of phthalocyanine (combustion with an excess of concentrated sulphuric acid) left no trace, *i.e.*, less than 0.001 mg. of ash.

When small amounts of phthalocyanine are sublimed in vacuo the deposit forms a lustreless green mass with no signs of crystalline structure under a magnification of 250-fold. In a number of experiments we have dissolved this deposit and recrystallised it into normal purple crystals. Since it was important to eliminate any traces of metals we carried out the distillation of some samples in quartz vessels and after sealing off the side tube from which the original crystals had been sublimed we dissolved the green phthalocyanine sublimate in quinoline which had been freshly distilled in quartz. The crystals obtained from this solution were washed with ether, also freshly distilled in quartz. Alternatively, benzophenone and alcohol (both distilled in quartz) were used instead of quinoline and ether respectively.

The hydrogen employed was purified by passing through palladium while the oxygen used was ordinary cylinder gas.

I. Atomic Interchange between Hydrogen and the Phthalocyanines.

When phthalocyanine or copper phthalocyanine is heated with hydrogen containing deuterium, an atomic interchange is observed between the hydrogen and the phthalocyanine. This is shown by the following experiments:

1. 100 mg. of phthalocyanine were heated for 16 hours at 377° C. in 150 c.c. of hydrogen (containing 7.07 per cent. D) at a pressure of 203 mm. At the end of this period the pressure was unchanged. The D-content of the hydrogen had dropped to 6.65 per cent.
2. Another 100 mg. of phthalocyanine were heated for 20 hours at 450° C. in 150 c.c. of hydrogen, $p = 170$ mm., D-content = 7.07 per cent. At the end of this period the pressure was again unchanged, while the D-content of the hydrogen had dropped to 5.97 per cent. The phthalocyanine distilled to the cool parts of the tube and deposited in purple needles. Some undistilled green residue (see previous section) remained

² Robertson, *J.C.S.*, 1935, 615.

in the heated part of the tube. 60 mg. of the purple crystals were combusted and the water formed showed 1.13 per cent. D-content. If the

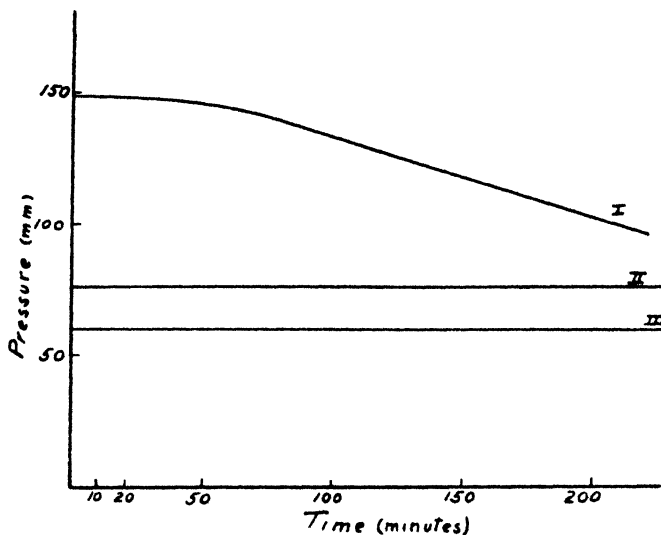


FIG. 1.

III. Blank (no catalyst) in Quartz at 300° C.

II. Blank (no catalyst) in Pyrex at 250° C.

I. Blank (no catalyst) in Pyrex at 350° C.

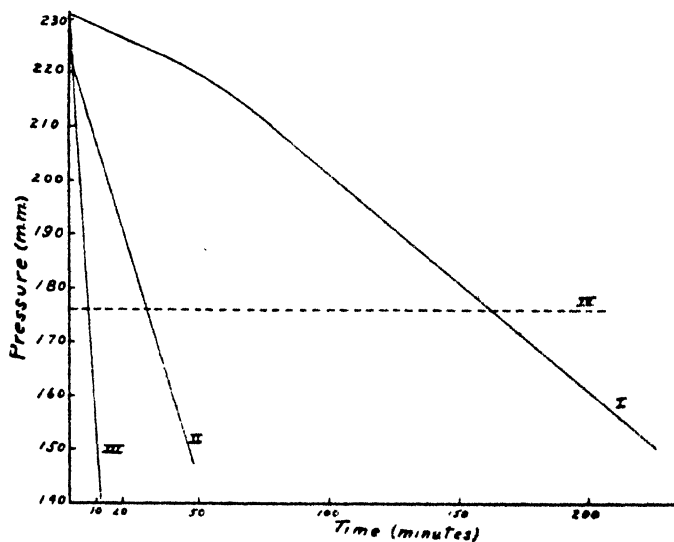


FIG. 2.

Three different samples of original material.

I. About 50 mg. crystalline phthalocyanine in Pyrex at 253° C.

II. About 50 mg. crystalline phthalocyanine in Pyrex at 276° C.

III. About 50 mg. crystalline phthalocyanine in Pyrex at 200° C.

IV. Expt. II., Fig. 1.

is certainly not restricted to the hydrogen atoms in the central ring.

3. 100 mg. of copper phthalocyanine were heated for 21½ hours at 404° C. in 150 c.c. of hydrogen containing 7.07 per cent. D at a pressure of 182 mm.

"distribution factor" for D between molecular hydrogen and organic hydrogen (in CH or NH) is assumed to be about unity the result indicates that 19 per cent. of the H-atoms in phthalocyanine participate in the exchange. Since the distribution factor is, in fact, more favourable to the organic hydrogen, it might be that only about 10 per cent. of the hydrogen atoms participate in the reaction, which could correspond to the two H-atoms in the central ring. The question whether H-atoms in this central ring are more (or less) readily exchanged than those attached to the four benzene rings cannot be decided yet. The fact that copper phthalocyanine also shows an interchange with molecular hydrogen proves that interchangeability

The pressure again remained unchanged and the D-content of the hydrogen fell to 6.81 per cent.

4. The same sample of 100 mg. of Cu phthalocyanine was heated for 25 hours at 500° C. in 150 c.c. of hydrogen containing 90 per cent. D, at 116 mm. pressure. The D-content of the hydrogen fell to 62.4 per cent. In the course of this experiment the substance distilled off and deposited in long purple needles on the cool parts of the tube. 60 mg. of the purple crystals were combusted and the water produced contained 12.6 per cent. D. Again, assuming a distribution ratio of unity, about 17 per cent. of the hydrogen atoms of the Cu phthalocyanine have taken part in an exchange reaction.

Further experiments which prove the interchange between the phthalocyanines and molecular hydrogen are to be found in the following section.

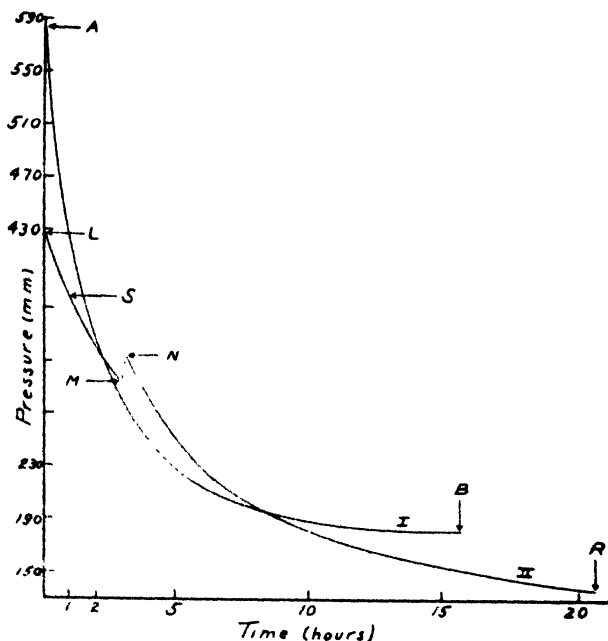


FIG. 3.

I. 100 mg. freshly sublimed phthalocyanine in quartz, $t = 293^{\circ}\text{C}$.

From analysis, partial pressure of oxygen at A = 135 mm.; at B = 1 mm.

Theoretical pressure drop corresponding to a stoichiometric combination of $\text{H}_2 + \text{O}_2$ is 402 mm.; observed pressure fall is 382 mm.; difference of 20 mm. due to water vapour. (No liquid air trap used.)

II. 50 mg. of phthalocyanine, sublimed in pyrex.

Portion LM, $t = 285^{\circ}\text{C}$.

Portion NR, $t = 345^{\circ}\text{C}$.

At L $p_{\text{O}_2} = 150$ mm.; at S $p_{\text{O}_2} = 134$ mm.

Theoretical pressure drop is 48 mm., observed pressure fall is 44 mm. (Liquid air trap used.)

II. Phthalocyanines Catalysing the Interchange between Hydrogen and Water.

The experiments described below show that the phthalocyanines are also capable of catalysing the atomic interchange between deuterium and water vapour.

A sample of the catalyst was heated in a sealed pyrex tube with 90 per cent. D_2 and 50–60 mg. of H_2O . After the experiment the density of the water, and in some cases the D-content of the remaining hydrogen as well as that of the phthalocyanine, were determined. The results are presented in the table.

The blank experiments show that while at a temperature exceeding to that any of the catalytic experiments a trace of interchange was present,

Catalyst.	Volume of Gas.	Pressure at 20° C.	Temperature of Reaction C.	Time, Hours.	Final D— of Gas.	D of Water.	D in Catalyst.
					Per Cent.	Per Cent.	Per Cent.
1. 100 mg. P.C.	130	162	360	19	72	5.98	0.82
2. 100 mg. P.C.	150	138	365	17.2	60.5	9.3	1
3. 100 mg. Cu. P.C.	155	161	353	21.5	—	1.39	—
4. Blank run.							
No catalyst	155	157	386	22	—	0.18	—
5. 100 mg. P.C.	155	147	255	48	—	12.5	—
6. Blank run.							
No catalyst	160	153	340	21.7	—	0.00	—
7. 100 mg. P.C.	155	152	200	21	—	1.9	—
8. 100 mg. Cu. P.C.	155	152	355	21.2	—	1.18	—

no exchange occurred in the range in which the catalytic experiments were performed.

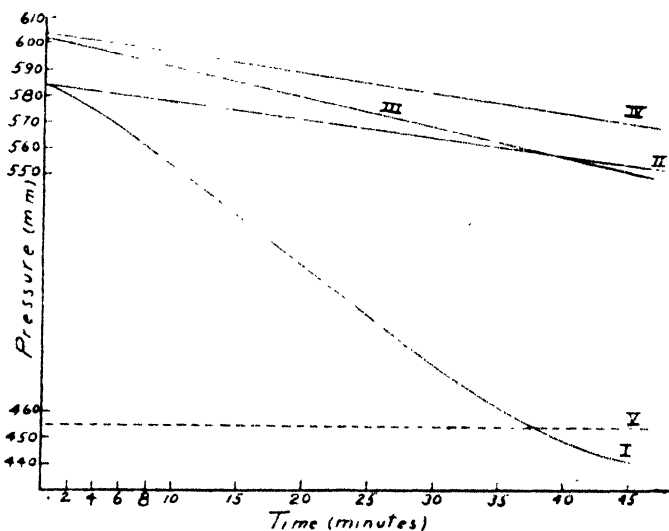


FIG. 4.

Temperature 202° C.; in Quartz.

- I. About 100 mg. freshly sublimed phthalocyanine. (Activity much greater than that of original samples.)
 - II. Sample I. on succeeding day. (Activity much reduced.)
 - III. Sample II. after recrystallisation from benzophenone and washed with alcohol.
 - IV. Another 100 mg. of phthalocyanine recrystallised from quinoline and washed with ether.
- (Operations mentioned for III. and IV. carried out in quartz, as described in text.)
- V. Expt. II. Fig. 1.

Experiments 1, 2, 5, and 7 show that the temperature coefficient of the catalysed reaction is small, corresponding to an activation energy in the vicinity of 6 K. Cals.

It is apparent from a comparison of experiments 3 and 8 with experiments 1 and 2, that the copper phthalocyanine as we have it is less active as a catalyst for the exchange be-

tween deuterium and water, than is free phthalocyanine.

III. Combustion of Hydrogen in Oxygen Catalysed by Phthalocyanines.

The formation of water from its elements is catalysed by phthalocyanines at temperatures between 250° and 370° C. The experiments were carried out by heating 50-100 mg. of free phthalocyanine or its copper derivative with mixtures of H₂ and O₂ in tubes of pyrex glass and in quartz vessels.

Out of a great number of experiments, a few representative examples are described below. Blank experiments showed that the reaction was very minute below 370°C . in the absence of a catalyst. The reaction never failed to proceed when crystalline phthalocyanine (purple) was used, but the microscopically amorphous green deposit produced by sublimation of phthalocyanine was erratic in its action. To test this deposit formed by sublimation, a vessel was used with a small side tube from which the material was distilled into the body of the vessel. Whatever residue remained was left in the side tube outside the heated zone. When larger quantities (100 mg.) of phthalocyanine are distilled in vacuo, it is possible to obtain a very active crystalline sublimate which easily loses most of its excess activity, however, during its catalytic action on the $\text{H}_2 + \text{O}_2$ reaction.

In several experiments a side tube immersed in liquid air was used to condense the water vapour formed. Nevertheless, a certain amount of

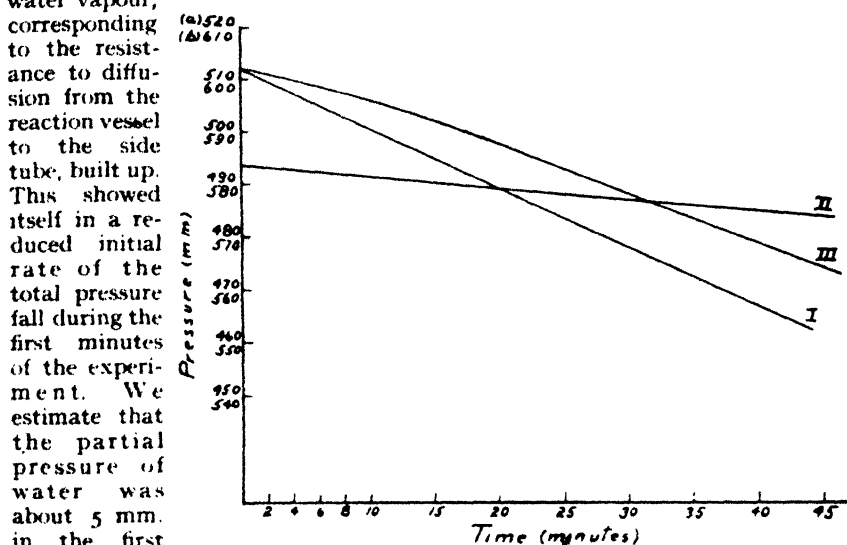


Fig. 5.

Sample III, Fig. 4; run at several temperatures.

I. At 293°C . Scale (b).

II. At 243°C . Scale (a).

III. Back again to 293°C . Scale (a).

ance to diffusion) fell off.

In order to test whether the H_2 and O_2 disappeared in stoichiometric amounts the gas was repeatedly analysed by measuring its density (after passing through a liquid air trap) with a quartz gas density balance.² The result showed that the pressure fall was actually due to a stoichiometric combination of H_2 and O_2 .

The analysis by gas density measurement is correct only if no gases are formed during the reaction which can pass the liquid air trap. The absence of such gases was demonstrated by passing the analysed gas over heated copper, copper oxide, when complete disappearance of the gas took place.

We found traces of a gas formed during the catalytic reaction which condensed in the liquid-air-cooled side tube and was released at solid CO_2 temperature. In general, no precautions were taken against contamination of the catalyst by the vapours of tap grease or mercury. Such precautions

² Whytlaw-Gray, Patterson, and Cawood, *Proc. Roy. Soc., A*, 1931, 134, 8.

are actually unnecessary since some experiments, in which such vapours were cut off by a liquid air trap, differed in no way from the others.

Fig. 1 shows a few blank experiments made in the pyrex tubes and quartz tubes actually used for the catalytic experiments. These curves are indicated by a dotted line in the later diagrams which represent various runs using phthalocyanine and copper phthalocyanine. The specific conditions of each experiment are indicated in the legend.

Fig. 2 shows the reaction on several different samples of phthalocyanine at a number of temperatures. In Fig. 3 are longer runs, one of which was carried to completion, *i.e.*, all the oxygen present consumed. The partial pressures of the oxygen, as obtained by analysis are indicated

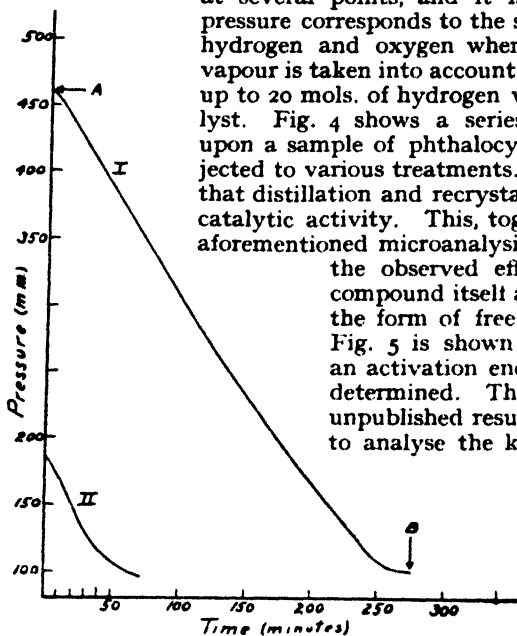


FIG. 6.

- I. 100 mg. crystalline copper phthalocyanine in pyrex at 270° C.
From analysis, partial pressure of O_2 at A = 124 mm.; at B ≤ 1 mm.
Theoretical pressure drop is 369 mm.; observed pressure drop is 360 mm. (Liquid air trap used.)
- II. 30 mg. crystalline copper phthalocyanine in pyrex at 360° C.

account of the possibility of oxidation and CuO , Cu , catalysis.⁴

IV. Experiments on Solution of Phthalocyanines and on Other Organic Compounds.

An attempt was made to find the exchange reaction between deuterium and phthalocyanine in solution. As solvent we used benzophenone at

⁴ No such objection can be raised against the reactions on copper phthalocyanine described in the preceding section, in which no oxygen was present. Dr. Linstead has stated in a private communication that no free metal should be present in either the phthalocyanine or the Cu -phthalocyanine with which he supplied us.

300° C., quinoline at 270° and 310° C. (in a sealed tube) and cold concentrated H_2SO_4 , in all cases with negative results. It seems that solvation blocks the catalytic centres of the phthalocyanine molecules.

These negative experiments demonstrate that quinoline and benzophenone certainly are incapable of reacting with molecular hydrogen. An experiment in which anthracene was heated for 20 hours at 300° with D_2 , also showed no exchange.

Summary.

1. Crystals of phthalocyanine and of copper phthalocyanine have the capacity to activate molecular hydrogen. (a) They show atomic interchange with molecular hydrogen. (b) They catalyse the atomic interchange between molecular hydrogen and water vapour. (c) They catalyse the formation of water from hydrogen and oxygen.

2. The activation energy of (b) is very small, in the vicinity of 6 K cal. The activation energy of (c) is larger, being about 18 K cal.

ACTIVATION OF HYDROGEN BY PHTHALOCYANINE AND COPPER PHTHALOCYANINE. PART II.

BY M. CALVIN, D. D. ELEY AND M. POLANYI

Received 25th June, 1936.

The conclusion reached in the previous paper that molecular hydrogen is activated by phthalocyanine compounds receives further support from the observation described below showing that *para*-hydrogen is converted into normal hydrogen by crystals of phthalocyanine and copper phthalocyanine. The rate of conversion was found to have a positive temperature coefficient, hence it is not a paramagnetic effect ("low temperature mechanism"), but must be due to a disruption of the hydrogen molecules ("high temperature mechanism").¹

Experiments and Discussion.

Three samples, I., II., III., of phthalocyanine were used. I. was the original material as obtained from Dr. Linstead. II. and III. are the same samples that were used in experiments IV., Fig. 4, and III., Fig. 4, respectively of the previous paper, *i.e.* substances distilled and recrystallised with special precaution. The *para*-conversion was carried out after the $\text{H}_2 + \text{O}_2$ experiments in the same vessels. Preliminary to the introduction of *para*-hydrogen the catalyst was baked out for an hour in vacuo at 300° C. The *para*-hydrogen, which was about 10 per cent. excess over the equilibrium concentration, was analysed by the micro method of Farkas² in the modified apparatus of Eley and Tuck.³ In the table the rates of conversion are expressed in terms of first order constants k . Evidence that the reaction is first order is given below.

From experiments 5 to 8 an activation energy of 5700 calories was derived (Fig. 1). Experiments 10 to 13, represented in Fig. 2, show the first order rate. Comparison of experiments 10-13 with 14, and of 8 with 9 show that a 20-fold change of pressure does not effect the rate constant.

¹ Bonheeffier, Farkas, and Rummel, *Z. physikal. Chemie, B.* 1933, **21**, 225.

² A. Farkas, *ibid.*, **22**, 344.

³ Eley and Tuck, this no, p. 1425.

TABLE.

No.	P_{H_2} Pressure, mm.	Temperature, C.	Time, Hours.	k , Hours ⁻¹ .
Sample I. 50 mg. phthalocyanine in a pyrex vessel (200 c.c.).				
1	8.0	252	16.4	0.133
2	8.0	196	3	0.062
Sample II. 100 mg. phthalocyanine, distilled in quartz vessels and recrystallised from quinoline in quartz.				
3	15	295	1.5	0.15
4	20	287	—	0.14 *
5	8.5	150	16.5	0.027
6	8.5	303	—	0.15 †
7	8.5	193	12	0.044
8	8.5	354	—	0.21 †
9	0.4	345	0.87	0.21
Sample III. 100 mg. phthalocyanine distilled in quartz vessels and recrystallised from benzophenone in quartz.				
10	8.5	285	0.52	0.27
11	8.5	285	1.35	0.22
12	8.5	285	2.67	0.21
13	8.5	285	4.0	0.21
14	0.3	278	3	0.18
14a	14 corrected to	285	—	0.23
Sample IV. 100 mg. copper phthalocyanine in quartz.				
15	19	285	3.25	0.13
Sample V. 150 mg. copper phthalocyanine in quartz.				
16	8.5	286	4.5	0.23
17	8.5	156	13.5	0.077
18	8.5	354	0.93	0.47

* Average of 3 analyses. These were taken by extracting small quantities of gas by means of a lock, at various times.

† Average of 4 analyses made at various times.

These observations conform with the assumption that the conversion is due to adsorption on a set of centres of uniform energy, the heat of desorption being — 5600 calories or less.

A comparison of the results on samples I., II., and III. shows that distillation and recrystallisation in quartz vessels, a process which might be expected to remove or at least greatly to reduce any traces of free metal originally present in the material, has no effect on the catalytic activity. We consider, therefore, that this activity is due to the pure organic substance.

The observed activation energy of 5700 calories is of the same order as the activation energies observed for the *para*-hydrogen conversion on metal surfaces. The fact that our conversion rates are slower than those obtained on metals is only partly due to the smallness of the active surface which is of the order of 10 cm.² (see previous paper). A comparison of the total number of molecules striking the surface having an energy greater or equal to 5700 calories with the actual number converted leads to a "steric factor" of 10⁻⁵. The reaction thus appears to have a very small entropy factor arising, no doubt, mainly from a very precise configuration of the transition state in co-ordinate space.

A few experiments carried out on copper phthalocyanine show that its action is very similar to that of free phthalocyanine. The two samples, IV., V., of copper phthalocyanine were the untreated original crystalline material as obtained from Dr. Linstead. The samples in quartz vessels were baked out at 330°C . in vacuo for about an hour. Both the amount of conversion expressed in the absolute value of the constants and the activation energy of about 5000 calories obtained from experiments 16, 17, 18, are quite similar to the corresponding data of phthalocyanine.

A certain amount of "low temperature" conversion is to be expected since copper phthalocyanine is paramagnetic,⁴ but the positive temperature coefficient indicates that at the temperatures under consideration the conversion proceeds predominantly through a disruption of the H—H bond as is the case with free phthalocyanine.

The activation energy involved in the activation of hydrogen by the phthalocyanine is so small that the processes arising from it should easily be observable at ordinary temperatures if the phthalocyanine could be spread out so as to present a large surface area. Experiments are in progress to realize this condition. A monolayer of 100 mg.

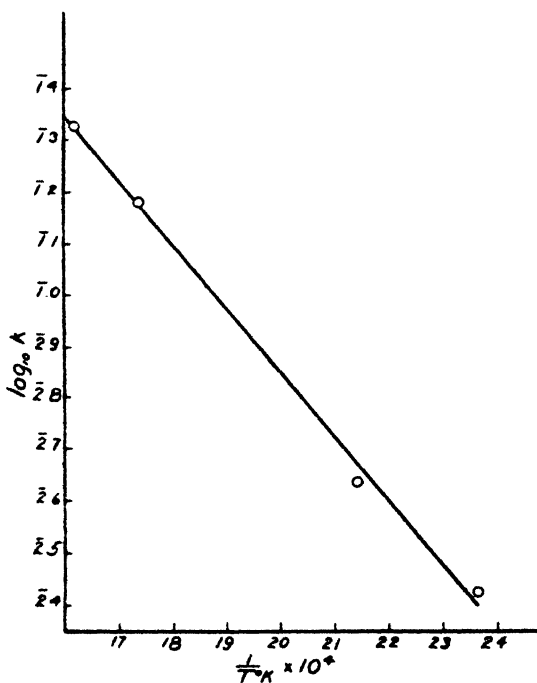


FIG. 1.

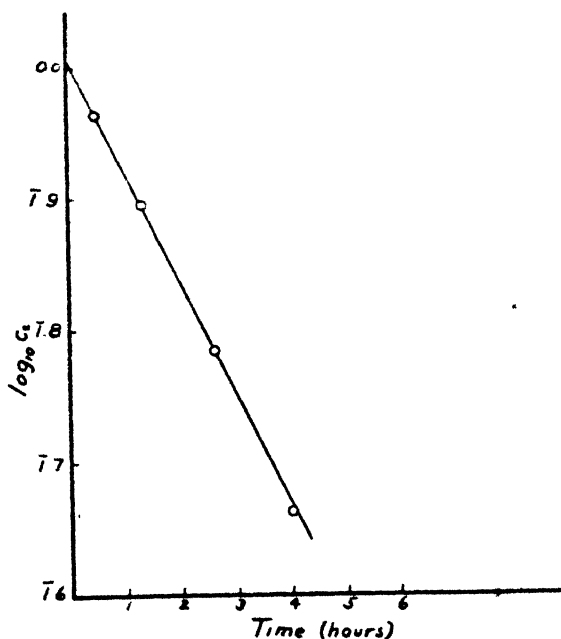


FIG. 2.

⁴ Klemm and Klemm, *Z. praktische Chemie*, 1935, 143, 82.

of phthalocyanine having an area of 10^6 cm.² would convert per second, at 40° C., 80 c.c. of *para*-hydrogen at the prevailing pressure. From a similar calculation based on the (quite provisional) figure of 17,500 calories for the activation energy of the $H_2 + O_2$ reaction catalysed by phthalocyanine we obtain an oxygen consumption of 25 c.c. for 100 mg. of catalyst.

These figures show that minute quantities of phthalocyanine spread out in a monolayer can activate hydrogen at body temperature at a rate far exceeding the rate of respiration; the actual burning of hydrogen, however, would be slower than the rate at which oxygen is consumed by the human body.

Although the positive temperature coefficient of the *para*-hydrogen conversion indicates that the reaction goes through a stage involving the disruption (weakening) of the H—H bond, this does not necessarily imply that the $H_2 + D_2 = 2HD$ reaction will go at the same rate, a correspondence which has been observed by Fajans on nickel surfaces.⁵ Such will be the case only if the mobility of the resulting H atoms on the phthalocyanine is so great that the probability of molecular desorption of any hydrogen atom with its original partner is not greater than the probability of desorption with another adsorbed hydrogen atom. In the case of the phthalocyanine it would seem that the probability of desorption of the original pair is great since the chemisorption of the hydrogen molecules may take place in the central squares formed by four nitrogen atoms of each phthalocyanine molecule. Such activating centres would be widely separated from one another, and there would be little chance of atomic interchange between pairs absorbed on different centres. Future experiments on the $H_2 + D_2$ reaction will elucidate this point.

It is to be expected that compounds related to the phthalocyanines also exhibit their capacity to activate hydrogen. Similar tests are being carried out on chlorophyll, haemin, and related compounds.

Summary.

1. Crystals of phthalocyanine and copper phthalocyanine catalyse the conversion of *para*-hydrogen into normal hydrogen.
2. The activation energy of the conversion on free phthalocyanine is 5700 calories, while that on copper phthalocyanine is about 5000 calories; the temperature independent factor is small and the first order constant is independent of pressure.
3. The positive temperature coefficient of the reaction shows that it involves a disruption of the H—H bond by chemisorption.
4. A few milligrams of a substance acting like phthalocyanine spread out into a monolayer could account for the rate of metabolism in the human body.

⁵ E. Fajans, *Z. physikal. Chemie, B*, 1935, **28**, 239.

POLAROGRAPHIC INVESTIGATIONS OF ANHYDROUS ACETIC ACID SOLUTIONS.

By D. MACGILLAVRY.

Received 30th June, 1936.

Over potentials can be conveniently studied experimentally, using the polarograph as designed by Heyrovsky,¹ especially as a single experiment gives a complete curve of the relationship between potential and current for the cell under investigation.

Though the specific influences of the cations present in aqueous solutions on the conduction of the current are well understood² the theoretical interpretation of many other details still remains doubtful.³ The difficulties arising in the theoretical interpretation result from the fact that we are dealing with systems not in thermodynamical equilibrium, so that in addition to the properties determining such equilibria, we have to take into account the velocities of all the possible mechanisms governing the conduction of the current.

Up to the present only aqueous solutions have been investigated with the polarograph. Much work has been done on the waves caused by cations and on the maxima caused by oxygen and other "surface active" substances. It is not known whether these polarographic characteristics are dependent only upon the solutes regardless of the solvent, or if marked changes will occur when working with the same solutes in other solvents. The importance of this question is apparent.

This paper describes some preliminary experiments with solutions in anhydrous acetic acid. The polarograms obtained reveal features which are quite distinct from the well-known phenomena shown by aqueous solutions.

Experimental.

Anhydrous acetic acid was prepared by adding borontriacetate in slight excess to 99.8 per cent. acetic acid and fractionating the mixture. This method has been described by Eichelberger.⁴ The anhydrous acetates were prepared by crystallisation from mixtures of acetic acid and acetic anhydride followed by recrystallisation from anhydrous acetic acid.⁵

All experiments were carried out with the dropping mercury cathode and a mercury anode. Most of the solutions were used in the ordinary small cells with flat bottoms giving a large anode area. In order to work with small volumes of solution a special cell was constructed (see Fig. 1). The use of an anode with a small area was possible, since with dilute solutions the currents were very small.

¹ M. J. Heyrovsky, *Bull. Soc. Chim. France*, IV, 1927, 41, 1224.

² J. Heyrovsky and D. Ilkovic, *Coll. Czechoslovak Chem. Communications*, 1935, 7, 198.

³ Recently D. Ilkovic has given a mathematical theory of the Maxima on current voltage curves, *ibid.*, 1936, 8, 170.

⁴ W. C. Eichelberger, *J. Am. Chem. Soc.*, 1933, 55, 3633.

⁵ I. M. Kolthoff and A. Willman, *ibid.*, 1934, 56, 1007.

The Nejedly galvanometer had a sensitivity of 9.29×10^{-8} amp. for 1 mm. deflection at a distance of 1 meter. The sensitivity was reduced when necessary with a Nejedly reductor box. In the actual set up the scale was 30 cm. from the galvanometer, so that 1 mm. along the current axis was equivalent to 3.1×10^{-8} amp. The series of parallel potential lines were 100 mm. long and 10.5 mm. apart in the original polarograms.

Since the simplest polarograms in water are obtained with the salts of heavy cations and stable anions, these experiments deal mainly with solutions of heavy cations in anhydrous acetic acid. It is of interest first to compare pure acetic acid and distilled water. The cations of both solvents are hydrogen ions. Hence, one might expect a gradual transition from the well-known polarograms of acid solutions to those of the pure solvents. This is not the case; at least no hydrogen waves or any changes due to deposition of hydrogen could be observed.

Very dilute solutions of HCl all give polarograms consisting of an almost horizontal part at lower voltages, a sudden break, and a logarithmically rising part at higher voltages. At still higher voltages the steeply rising part flattens off to the saturation current. With one particular cell a polarogram was first taken with the sensitivity of the galvanometer reduced to 1/100. Then, after addition of KCl another polarogram was

taken. The conductivity had increased so much, that the sensitivity of the galvanometer could be reduced to 1/2000. A hydrogen wave could no longer be traced, the amount of hydrogen ions being too small to be detected with the lower sensitivity. The polarogram showed only the usual potassium wave.

Next, a polarogram of a cell filled with distilled water was taken with sensitivity 1/10. The curve obtained is a nearly straight line, only slightly curved over the whole length, being convex to the voltage axis. The polarogram shows no break nor waves throughout the whole voltage range up to 3.8 volts. No special surface phenomenon is revealed. It is interesting to note that the oscillations caused by the dropping mercury cathode increase proportionally with the total current intensity.

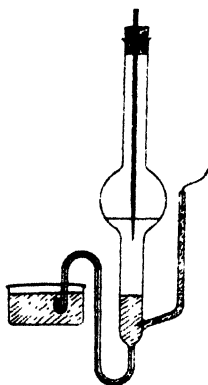


FIG. 1.

Anhydrous acetic acid is a very poor conductor. Therefore the cathode was placed at very small distance from the large anode surface, the distance being kept just large enough to prevent the mercury droplets from touching the anode. With this cell, even using the highest sensitivity, only a very slight deflection of the galvanometer, increasing with the voltage, was observed.

It is evident from these observations, that the acetic acid, like water, contributes very little to the conductivity of the solutions at all voltages and that all waves and other specific phenomena are caused by the dissolved substances. This does not mean that the solvent cannot have a great influence on the general appearance of polarograms, as we shall have occasion to note.

Acetic Acid Solutions of one Electrolyte.

All the acetic acid solutions investigated behave quite differently from aqueous solutions, in that it was never necessary to free them from dissolved oxygen, so that the ordinary precautions to exclude oxygen from the solutions were quite superfluous. The appearance of an oxygen maximum in some of the polarograms was probably due to the presence of oxygen together with traces of water; such maxima could be made to vanish by passing nitrogen through the cell.

A second interesting peculiarity is that all polarograms obtained with dilute solutions are almost perfectly straight lines (Fig. 2). The oscillations

caused by the cathode always increase proportionally with the total current. This was observed with the dilute solutions of HCl , LiCl , NaCH_3CO_2 and with the saturated solutions of $\text{Cu}(\text{CH}_3\text{CO}_2)_2$ and $\text{Cd}(\text{CH}_3\text{CO}_2)_2$. This behaviour suggests that the slowest process determining the rate of electric conduction takes place in the interior of the solutions, probably partly because of the high resistance. However, the entire absence of waves characteristic for the cations is very remarkable. The polarograms of these dilute solutions are similar to those obtained with acetic acid and water, in this respect that no waves are found, although the dilute solutions in acetic acid have a higher conductivity than that of the pure solvent. The sensitivity of the galvanometer was reduced, for instance, to $1/4$ with the saturated solution of $\text{Cu}(\text{CH}_3\text{CO}_2)_2$.

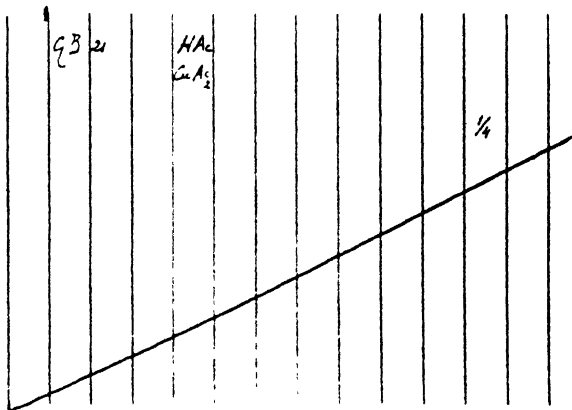


FIG. 2.

With more concentrated solutions of NaCH_3CO_2 the following observations were made (Fig. 3). At voltages up to 2 volts the current density increased slowly. At about 2 volts the polarograms show a sudden bend, apparently caused by the Na^+ ions. At still higher voltages the curve is almost perfectly straight, the slope being greater than at voltages below 2 volts. This section of the polarogram is different from that obtained in aqueous solution, since the change in current is proportional to

the increase of voltage, whereas in aqueous solution the relationship is a logarithmic one. Furthermore, even at 7.6 volts no indication of a saturation current could be detected.

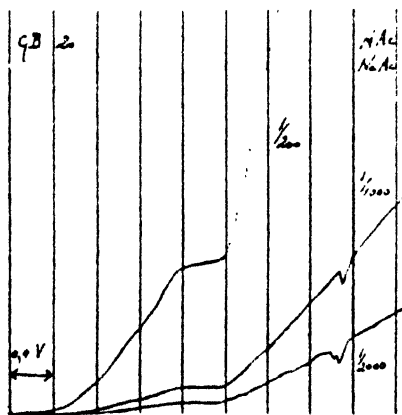


FIG. 3.

Thus, in acetic acid solution the characteristic potential for Na^+ ions cannot be derived in the manner proposed by Heyrovsky,² unless the potential giving half the diffusion current has a much higher negative value than the corresponding potential in aqueous solutions. This, however, would produce a theoretical difficulty, because the potential of the 45° tangent point (the sharp bend) would have to shift much more upon dilution than would follow

from Heyrovsky's formula. The increase in current density below 2 volts is not quite proportional to the voltage; there is a little more rapid increase between 0.4 and 1.6 volt. This can be attributed to a mercury wave. Mercury could be detected in solution afterwards.

No mercury wave can occur when chlorine ions are present in solution. This was demonstrated in the following way. A solution of HgCl_2 in acetic acid was shaken with mercury. Then, the solution was decanted

from the heavy precipitate of Hg_2Cl_2 into a cell for investigation. The polarogram was taken with the highest sensitivity and again was a nearly straight line, with a very slight slope (Fig. 4). These systems are complicated, however, by the precipitation of calomel in all solutions containing

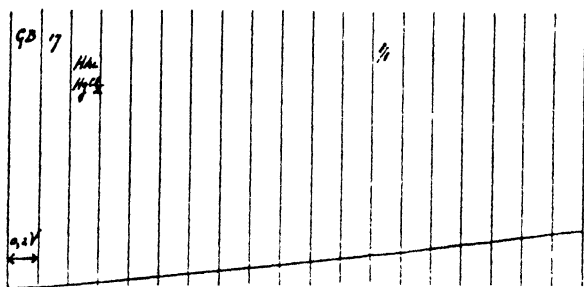


FIG. 4.

chlorine ions, whenever the voltage is increased above 1.8 volts.

Since the characteristic features in polarograms are only shifted but not changed by varying the concentrations within reasonable limits, it appears desirable to describe these results,

though they are of a qualitative nature only. We wish to extend the investigation to solutions containing several cations and to check the present results quantitatively, giving special attention to the transition from the polarograms of dilute solutions to the more concentrated solutions.

Summary.

A first report has been given on polarographic investigations with the dropping mercury cathode of solutions of anhydrous acetic acid.

Oxygen does not cause maxima in the complete absence of water.

The polarograms of dilute solutions are practically straight lines, showing no waves or breaks characteristic of the ions in solution.

The polarograms of a more concentrated solution of NaCH_3CO_2 show a sharp bend at about 2 volts and a straight continuation above 2 volts. The small wave below 2 volts may be due to mercury.

The polarograms obtained are discussed and compared with the polarograms of aqueous solutions and of the pure solvents water and acetic acid.

My thanks are due to Professor J. Gillis for his kind interest in this work and to the Dutch Committee for intellectual co-operation between the Netherlands and Belgium for a grant.

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THE KINETICS OF THE THERMAL DECOMPOSITION OF ALKYLENE OXIDES. I. ETHYLENE OXIDE.

BY H. W. THOMPSON AND M. MEISSNER.

Received 3rd July, 1936.

The desirability of examining the kinetics of the homogeneous thermal decomposition of the vapours of a series of related compounds has recently been frequently emphasised. Hinshelwood and his collaborators have for example studied the relationships with aldehydes and ketones,¹ and with ethers, while Steacie and others have examined the series of alkyl nitrites.² Interest in the problem has increased as a result of certain hypotheses which have been suggested with regard to the mechanism of the reactions involved. On the one hand, the intervention of reaction chains in the processes has been considered, free alkyl radicals playing an important part in the propagation of the chains;³ on the other, there has been the discovery of the segmented nature of the curve connecting the "unimolecular" velocity constant for the decomposition of a particular substance with the initial concentration employed.⁴ This result has been interpreted as perhaps being connected with a localisation of the energy of activation in different parts of the same molecule, or with different types of activated state, with the consequence that a decomposition giving similar products may occur via independent mechanisms.

A comparison of the data with a homologous series of aldehydes has proved interesting as a means of suggesting the particular linkages or modes of vibration in which the energy of activation may become localised. It seemed therefore fitting to study the relationships with another series of homologues, the alkylene oxides, many of the simplest of which are very volatile and suitable experimentally. The present paper deals with the simplest member of the series, ethylene oxide. The data for propylene oxide, which shows significant differences of detail, will be given later.

The kinetics of the thermal decomposition of ethylene oxide have been studied previously by Heckert and Mack.⁵ The reaction was found to be homogeneous over the temperature range 380-444° C., giving as products carbon monoxide, methane, and a little hydrogen and ethane. Making corrections for a noticeable induction period, the course of the reaction could be represented by a "first order" equation, and over the range of pressure used (100-1000 mm.), the velocity constant was sufficiently independent of initial pressure to indicate an essentially first order process. On the other hand, a "falling-off" with decreasing initial

¹ *Proc. Roy. Soc., A*, 1926, **111**, 245; 1926, **113**, 221; 1933, **141**, 41; 1934, **146**, 345; 1935, **149**, 340, 355.

² *J. Chem. Physics*, 1934, **2**, 345; 1935, **3**, 344.

³ Rice and Herzfeld, *J. Am. C. S.*, 1934, **56**, 284, and a later series of papers.

⁴ Fletcher and Hinshelwood, *Proc. Roy. Soc., A*, 1933, **141**, 41; Hinshelwood, Fletcher, Verhoek and Winkler, *ibid.*, 1934, **146**, 327.

⁵ *J. Am. C. S.*, 1929, **51**, 2706.

concentration was noticed, but not examined in detail. The energy of activation was ca. 52,000 cal.

Heckert and Mack interpreted the induction period as involving, in part, a primary isomerisation to acetaldehyde, and from the retarding influence of many inert gases inferred the presence of reaction chains. A considerable alteration in the surface-volume ratio of the reaction vessel, did not, however, affect the reaction velocity.

On the basis of the data of Heckert and Mack, and assuming that at the highest initial pressures used by them the truly unimolecular course of the reaction had not yet been reached, Ramsperger⁶ calculated the number of squared terms between which the energy of activation must be divided, and found it to be greater than 14.

The results given below are in almost complete agreement with those of Heckert and Mack. They go further, however, and provide additional knowledge concerning the mechanism of the reaction. It is possible to measure the rate of the reaction up to temperatures some fifty degrees higher than the highest used by Heckert and Mack, and the complications introduced by the induction period are thereby largely eliminated; the possibility of interference by surface processes is also relatively decreased. More important, however, is the result that the "falling-off" of the velocity constant with decreasing pressure is rather more noticeable at the higher temperatures.

Several theoretical discussions of the reaction have recently been published. Kassel⁷ has contended that the mechanism proposed by Heckert and Mack is untenable since the acetaldehyde formed by a primary isomerisation would decompose much more rapidly than actually occurs. Fletcher⁸ has suggested that ethylene oxide undergoes two simultaneous primary reactions, one an isomerisation to give acetaldehyde, the other a decomposition to give free radicals, which then catalyse the decomposition of the aldehyde. This interpretation has been treated mathematically by Sickmann,⁹ who has thus obtained a qualitative explanation of the induction period and has interpreted the retarding influence of foreign gases as resulting from their power of facilitating the recombination of free radicals. These several hypotheses are discussed below.

Experimental Method.

The reaction was followed by measurement of the pressure change at constant volume. The apparatus and general procedure were similar to those previously described in the investigation of other similar decompositions.¹⁰ The reaction vessel was a cylindrical pyrex bulb of ca. 250 c.c. capacity, enclosed within an electric furnace. Temperature was measured by means of a platinum-platinum rhodium thermocouple in conjunction with a previously calibrated galvanometer. The reaction vessel was connected to a capillary mercury manometer, and via taps to a vessel containing liquid ethylene oxide, and to other containers of inert gases. The whole system could be evacuated by means of a Hyvac oil pump backing a mercury vapour pump. For the experiments in packed bulbs a cylindrical pyrex vessel containing many lengths of pyrex glass tubing was used, the relative surface-volume ratio of the packed and empty vessels being about eight-fold.

⁶ *Chem. Rev.*, 1932, 10, 27.

⁷ Kassel, *Homogeneous Gas Reactions*, 1932, p. 284.

⁸ *J. Am. C. S.*, 1936, 58, 534.

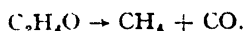
⁹ *J. Chem. Physics*, 1936, 4, 297.

¹⁰ Compare *J.C.S.*, 1935, 1443.

The ethylene oxide was a Kahlbaum product, refractionated in vacuo, the middle fraction being used. A second sample supplied by British Drug Houses Ltd. was fractionated, and gave the same results.

Products and End-Points.

According to Heckert and Mack, ethylene oxide decomposes, giving exactly 100 per cent. increase in volume. The temperature at which this measurement was made is not recorded, and it is assumed that at all the temperatures used, *i.e.*, up to 445°C ., and for all initial pressures, the pressure is exactly doubled at the completion of the reaction. Our measurements do not agree with this. At low temperatures and with low initial pressures, the pressure increase observed was ca. 100 per cent., but this decreased with increasing temperature or increasing initial pressure, so as to fall to below 80 per cent. at the highest temperatures and with the highest initial pressures. This is apparently to be explained by the occurrence simultaneously with the decomposition of a condensation process, the extent of which is increased as the pressure or temperature is increased. Such concurrent condensation reactions are common to analogous decompositions. A dark solid product is formed in the reaction vessel at high temperatures, which subsequently slowly decomposes. As the analyses given below show, the bulk of the decomposition follows the equation :



A pressure increase of 90 per cent. implies that 95 per cent. of the ethylene oxide decomposed according to this main reaction. For the purpose of the kinetic measurements, it was therefore necessary to construct calibration curves from which the "end-point" could be read off for any initial pressure at a given temperature.

The gaseous products of the decomposition are primarily methane and carbon monoxide, with a little hydrogen and ethane, agreeing with the results of Heckert and Mack.

That the reaction is, to a first approximation at least, uniform over the course of the pressure change, is shown by the analysis of the products at different stages of a run. Table I. shows typical data. Almost negligible traces of unsaturated hydrocarbons are included in the figures given for carbon dioxide.

The "residue" in each case was examined by combustion. The results are summarised in Table II.

The results in each case indicate that the residue is a hydrocarbon $\text{C}_n\text{H}_{2n+2}$, *i.e.*, methane or a mixture of methane with hydrogen and ethane with the last two in equal proportions.

TABLE I.—TEMPERATURE, 462°C . INITIAL PRESSURE, 300 MM.

	Per Cent. Age Total Pressure Change.	Per Cent. CO_2 .	Per Cent. CO .	Per Cent. "Residue."
(1)	25	0.2	49.8	50.0
(2)	25	0.0	50.1	49.9
(3)	50	1.5	48.5	50.1
(4)	60	0.2	49.8	50.0
(5)	95	0.1	50.6	49.3
(6)	100	1.0	49.5	49.5

TABLE II.

	Volume of "Residue" Taken.	Contraction on Combustion.	Carbon Dioxide Formed.
(1)	2.40	4.75	2.30
(2)	2.65	5.25	2.40
(3)	3.10	6.40	3.00
(4)	3.33	6.82	3.20
(5)	2.35	4.50	2.25
(6)	2.7	5.25	2.80

That the alteration in the percentage pressure increase at different temperatures is not, primarily at least, connected with a marked change in the nature of the reaction, but due to different degrees of superposed condensation, is shown by the analysis of the end-products at different temperatures, using the same initial pressure in each case. Table III. gives typical data.

TABLE III.—INITIAL PRESSURE, 300 MM.

Temperature °C.	CO ₂ .	CO.	"Hydrocarbon Residue."
492	0.0	49.9	50.1
462	0.5	50.5	49.0
442	0.3	50.0	49.7

TABLE IV.—TEMPERATURE, 492° C.

Initial Pressure, mm.	CO.	H ₂ .	C ₂ H ₄ .	CH ₄ .
30	49.2	7.7	7.7	35.4
30	50.5	6.7	6.7	36.1
340	49.9	4.3	4.3	41.5
392	50.3	4.65	4.65	40.5

The end-products using different initial pressures at the same temperature were also analysed. The hydrocarbon residue was combusted fractionally, first with copper oxide to estimate hydrogen, and then with oxygen to estimate methane and ethane. From the data of Table IV. it is seen that at the lowest initial pressures there may be a slight increase

in the relative proportions of ethane and hydrogen to methane.

In view of the possibility that the process may involve a primary isomerisation to give acetaldehyde, qualitative tests were made for the latter. The gaseous products were withdrawn at different stages of a run into a large evacuated pipette, and shaken with water. The solution was treated with Schiff's reagent. No trace of acetaldehyde could be detected at any stage of the reaction over the range of temperatures used. This result agrees with that of Heckert and Mack.

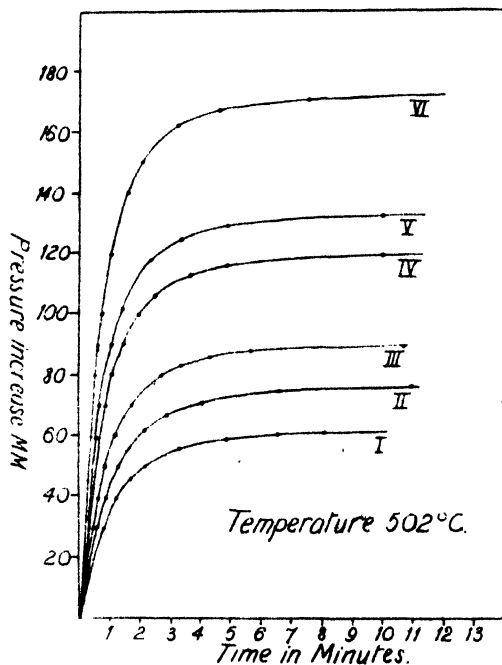


FIG. 1.

The Homogeneity of the Reaction.

The homogeneity of the process was tested by comparison of the rate in a packed and unpacked vessel. In the packed vessel the reaction, which proceeds to almost the same "end-point" as in the empty vessel, is slightly retarded, but the retardation is such as to correspond to only two or three degrees centigrade change of temperature. Fig. 1 shows the period of half-change plotted as a function of pressure at 457° C. in the two vessels respectively. At 300 mm. initial pressure the ratio $t_{\text{packed}} : t_{\text{unpacked}}$ is 1.15. It is clear

that no appreciable surface reaction is involved, and if noticeably long reaction chains were propagated, a much greater retardation in the packed vessel might be expected.

The Order of the Reaction over its Course.

The general course of the reaction is exhibited by the curves of Fig. 2. The induction period noticed at lower temperatures by Heckert and Mack is less marked at the higher temperatures. There is no doubt that over its course the reaction follows essentially a first-order law. The constant $k = \frac{2.3}{t} \log \frac{a}{a-x}$ (k in sec^{-1} , is not, however, strictly constant, but increases slightly in the early stages and falls off in the later stages of a run. In the same way the ratio $t_1 : t_2$ is not exactly 2, but has a value lying between that of a first and second order change. Table V. gives typical data.

The initial increase in the value of k is clearly associated with the induction period; the falling-off in the later stages may be due to two causes, either first to the quasiunimolecular character of the decomposition, or secondly to the retarding influence of the products, which may behave like inert gases in the sense described below.

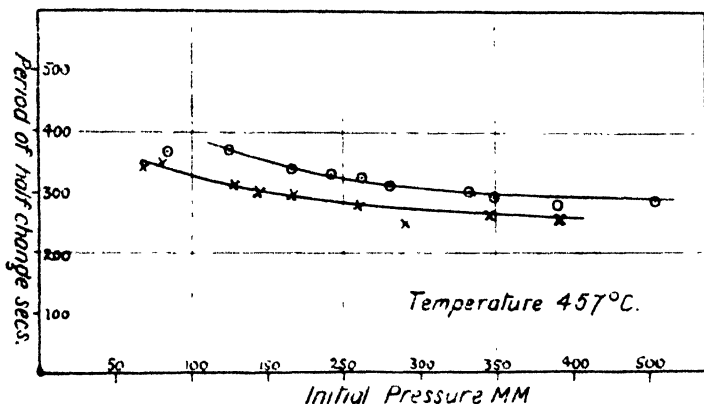


FIG. 2.

The evaluation of what may be taken as the "accurate" value of the quasiunimolecular velocity constant k is obviously therefore difficult. Heckert and Mack were able to "correct for" the induction period by assuming the primary isomerisation to acetaldehyde, although no experimental evidence for this was forthcoming. This treatment of Heckert and Mack is not entirely satisfactory. In order to account quantitatively for the course of the pressure change over an entire run, and obtain a differential equation to represent the rate in terms of the concentration and certain constants, it would be necessary to take into account all the various factors influencing the rate, a quantitative estimate of some of which is undeterminable. The value of k becomes fairly steady during the middle part of a run. For the purpose of the considerations of the succeeding sections, this value of k is taken as representing the "unimolecular" constant. As an indication of the close agreement with the results of Heckert and Mack, they find at 442°C. , $k = 0.0011$; the present method gives from our data $k = 0.0012$.

The value of the reciprocal of the period of half-change might also be taken as representing a measure of the unimolecular velocity constant, although the complex nature of the course of the reaction makes such a procedure rather doubtful. In fact, however, the value obtained for k by

the above method, agrees well with in general with that, calculated from $\frac{t-2}{t_4} \log 2$.

The Relationship between the Value of k and Initial Pressure.

Heckert and Mack noticed a decrease in the unimolecular velocity

TABLE V.—TEMPERATURE 462° C.

t secs.	Δp .	$k \times 10^3$.	t secs.	Δp .	$k \times 10^3$.	t secs.	Δp .	$k \times 10^3$.
1. Initial pressure, 310 mm.			2. Initial pressure, 212 mm.			3. Initial pressure, 100 mm.		
21	15	2.37	24	10	2.46	20	3	1.79
30	24	2.69	30	14	2.78	30	5.5	2.08
35	30	2.90	40	19	2.87	42	8	2.07
45	38	2.90	52	25	2.98	52	10	2.39
57	50	3.08	60	28	2.94	63	13	2.64
60	52	3.06	70	33	3.00	74	15	2.62
70	61	3.13	80	37	3.00	89	18	2.67
80	70	3.20	85	40	3.06	100	20	2.67
90	78	3.22	90	42	3.00	110	22	2.68
100	86	3.22	100	46	3.06	116	23	2.70
120	100	3.23	120	54	3.08	126	25	2.75
130	108	3.23	138	60	3.00	140	27	2.73
140	114	3.22	150	65	3.09	160	30	2.71
159	125	3.23	185	75	3.04	170	32	2.76
170	132	3.23	200	80	3.07	184	33	2.67
187	140	3.22	210	82	3.03	200	25.5	2.69
200	146	3.18	224	85	2.99	230	39	2.69
207	150	3.20	265	95	2.96	250	41	2.62
253	170	3.14	343	110	2.62	270	43	2.65
294	185	3.08	∞	174	—	300	46	2.60
342	200	3.01	$k = 3.07 \times 10^{-3}$			340	50	2.60
∞	310	—				389	53	2.50
$k = 3.23 \times 10^{-3}$						∞	85	—
						$k = 2.70 \times 10^{-3}$		
4. Initial pressure, 53 mm.			5. Initial pressure, 31 mm.			6. Initial pressure, 14 mm.		
29	3	2.26	40	2	1.95	34	0.5	1.24
47	5	2.38	55	3	2.14	62	1.0	1.42
75	8	2.48	78	4	2.09	100	2.0	1.72
100	10	2.38	95	5	2.15	173	3	1.66
110	11	2.41	121	6	2.07	230	4	1.74
135	13	2.39	140	7	2.14	328	5	1.64
157	15	2.43	165	8	2.11	411	6	1.68
190	17	2.37	193	9	2.09	643	8	1.70
235	20	2.34	217	10	2.11	∞	12	—
270	22	2.34	245	11	2.12	$k = 1.7 \times 10^{-3}$		
334	25	2.26	280	12	2.09			
390	27	2.19	311	13	2.10			
473	30	2.14	354	14	2.05			
540	32	2.12	390	15	2.08			
900	39	1.96	558	18	1.96			
1500	44	1.84	1140	24	1.93			
1800	45	1.82	1380	25	1.88			
∞	47	—	∞	27	—			
$k = 2.40 \times 10^{-3}$			$k = 2.11 \times 10^{-3}$					

constant with decreasing initial pressure, but did not examine it in detail. Table VI. gives the complete data for runs at 462° C.

It is seen that between 400 mm. and 20 mm. there is a decrease of k by about 30 per cent. The decrease observed by Heckert and Mack at lower temperatures over the same range of pressure was about 20 per cent.

The plot of k against p_0 (Fig. 3) reveals a relationship between the two quantities more complex than has hitherto been assumed. Above 250 mm. k is almost independent of p_0 , corresponding to a unimolecular process, although there are signs that k still tends to rise slightly with increasing pressure. Below 250 mm. initial pressure the plot of k against p_0 is "segmented" in nature. Between 250-40 mm. there is one roughly "bimolecular" segment, and below 40 mm. at least one other.

The plot of $1/t_4$ against p_0 gives a curve closely similar in form to that

of Fig. 3, and this result is reproduced at any temperature, but rather more pronounced at the higher ones.

Temperature Coefficient and Energy of Activation.

Table VII. summarises the value of k at different temperatures and for each of four different initial pressures. The logarithms of k are also given.

From the plot of $\log k$ against $1/T$ for each pressure the following values for the energy of activation are obtained :

At 400 mm. $E = 53,000$ cals.

At 50 mm. $E = 50,000$ cals.

Corrections have been made in each case for the variation of collision frequency with temperature.

Molecular Statistics.

To a very large extent at least, the decomposition can be regarded as a quasi-unimolecular reaction of the conventional type. The velocity of the reaction in the region of initial pressure above that at which the constant begins to "fall off," is far in excess of that to be expected from the expression (collision frequency $\times e^{-E/RT}$). Assuming that the energy of activation is distributed among n squared terms, n can be calculated as follows.

TABLE VI.

Initial Pressure, mm.	$k \times 10^3$.	Initial Pressure, mm.	$k \times 10^3$.
554	3.35	120	2.76
529	3.45	116	2.70
520	3.28	113	2.85
501	3.22	108	2.74
497	3.24	100	2.7
449	3.26	89	2.65
375	3.23	83	2.5
347	3.3	62	2.5
315	3.15	60	2.46
280	3.25	53	2.4
279	3.20	40	2.19
223	3.15	38	2.15
212	3.06	34	2.2
177	3.1	34	2.1
175	2.9	31	2.11
168	3.0	26.5	2.2
164	3.05	22	2.1
163	2.92	18	1.9
155	3.0	15	1.62
150	2.9	14	1.7
144	2.8	12	2.0
138	2.8	7	1.6
129	2.8	—	—

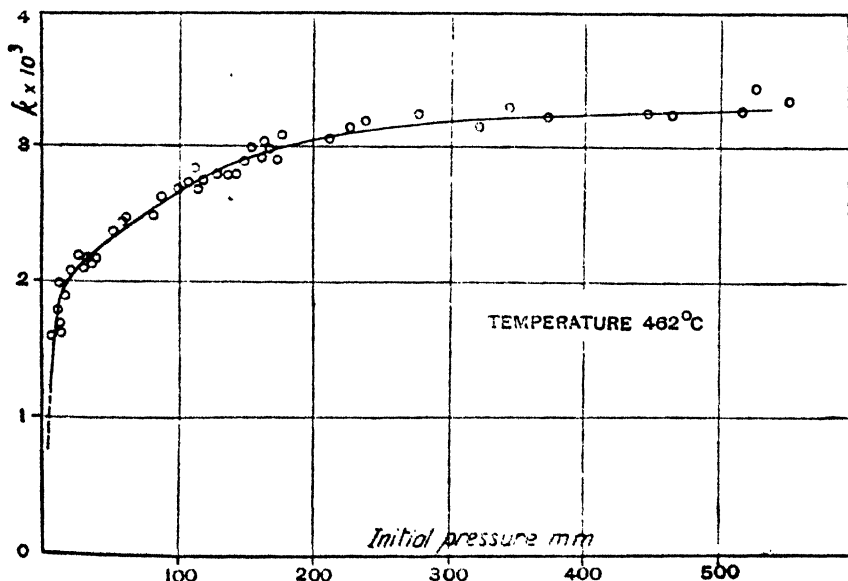


FIG. 3.

The unimolecular velocity constant at 462° C. and 300 mm. pressure (at which the falling off begins to be noticed) is $k = 3.22 \times 10^{-3}$ sec.⁻¹.

TABLE VII.

Temperature °C.	$1/T \times 10^3$	Initial Pressure mm.			
		400.	200.	100.	50.
422	1.439	0.42 4.0232	0.41 4.6128	0.38 4.5798	0.32 4.5051
442	1.399	1.22 3.0804	1.18 3.0719	1.04 3.0170	0.92 4.9638
452	1.379	2.03 3.3075	1.9 3.2788	1.68 3.2253	1.50 3.1761
462	1.361	3.27 3.5145	3.1 3.4914	2.65 3.4232	2.32 3.3655
472	1.342	5.5 3.7404	5.3 3.7243	4.4 3.6435	3.6 3.5563
482	1.325	8.8 3.9445	8.5 3.9294	7.0 3.8451	6.0 3.7782
492	1.307	—	—	10.1 2.0043	8.7 3.9305

and the energy of activation is 53,000 cal. The number of molecules reacting per c.c. per sec. is thence found to be 1.3×10^{16} .

The number of collisions between molecules per c.c. per sec. at the above temperature and pressure is $2.5 \sqrt{2} \pi \sigma^2 \bar{u} n^2 = 1.77 \times 10^{28}$; the number of activated collisions, assuming two squared terms are involved, per c.c. per sec. is then 3.7×10^{12} . Thus, the discrepancy is about 3500 fold.

Writing $\frac{(E/RT)^{1/n} - 1}{\frac{1}{2}n - 1} = 3500$, we find $n = 8$. This value is reasonably in agreement with the structure of the molecule, and perhaps more so than the value calculated by Ramsperger from the data of Heckert and Mack.

The Influence of Added Inert Gases.

It has in the past appeared somewhat surprising that the rates of the homogeneous gaseous decomposition of simple organic molecules such as aldehydes and ketones are, in general, unaffected by the addition of inert gases, especially if "collision" mechanisms underly the process of activation. Hydrogen has been found to possess in some cases the specific power of restoring the rate in the "low pressure bimolecular" region of a quasiunimolecular reaction to the "high pressure unimolecular" value. According to the original chain mechanism of Christiansen and Kramers, inert gases should behave as negative catalysts in the sense that they should lead to a deactivation of activated molecules on collision, but no evidence for such a property has been forthcoming. On the contrary, chain reactions are usually accelerated by the addition of diluent gases, probably since they prevent the diffusion of active centres to the vessel walls where these can be destroyed.

For these reasons, the influence of inert gases upon the rate of the decomposition of ethylene oxide is anomalous. The presence of the reaction products (carbon monoxide and hydrocarbons) or of argon or nitrogen reduces the rate of the decomposition. The effect of the products may contribute towards the observed decrease in the first order constant in the later stages of a run. Our results agree essentially with those of Heckert

and Mack; but a more detailed study is desirable, and only the main outlines will be given.

With pressures of diluent (argon, nitrogen, carbon monoxide) of the same order of magnitude as the pressure of ethylene oxide, the velocity constant is reduced by about 10-20 per cent. There seems to be a rough proportionality between the extent of the retardation and the pressure of added inert gas.

Table VIII. shows the effect of products upon a run at 460° C.; p_1 is the initial pressure of ethylene oxide, p_2 that of products.

Table IX. shows the effect of argon at 460° C.

TABLE VIII.

Pressure Increase, mm.	(1) $p_1 = 192$ mm. $p_2 = 0$ mm.	(2) $p_1 = 192$ mm. $p_2 = 100$ mm.
	Time in Secs.	Time in Secs.
10	24	31
20	50	59
30	74	87
40	103	117
50	135	150
60	168	188
70	205	228
80	247	279
90	300	339
100	360	414

TABLE IX.

Initial Pressure of Ethylene Oxide in mm.	Pressure of Argon Added in mm.	Time in Secs. for Pressure Increase of 40 Per Cent. Initial Pressure.
225	0	235
	50	240
	100	257
	200	267
192	0	244
	50	255
166	0	247
	100	258
	196	265
124	0	263
	200	282
	300	329

The addition of hydrogen was found to increase the velocity of the decomposition of ethylene oxide, in agreement with the results of Heckert and Mack. The important result, however, was that with initial pressures of ethylene oxide corresponding to the "bimolecular" region, the rate could be increased to values greater than that in the "unimolecular" region. It is not possible to draw significant conclusions from this, however, since in the presence of hydrogen the main reaction appears to be affected in nature, the "end-point" being different.

General Discussion.

The decomposition of ethylene oxide is, in broad outline, like other quasi-unimolecular decompositions. The number of squared terms among which the energy of activation must be distributed in order to comply with the measured rate is reasonable. The velocity constant decreases with decreasing initial pressure in the manner recently found in other similar reactions, and this phenomenon suggests that different types of activated state are possible. Until further data are available for other alkylene oxides it may be unwise to develop this hypothesis further.

There are nevertheless certain complications, such as the induction period, or the influence of added inert gases, which indicate that the relationships may not be so simple as the above implies. The hypothesis suggested by Fletcher and developed by Sickmann supposes that

acetaldehyde is formed by isomerisation, and concurrently with it are produced a few free radicals, which catalyse the decomposition of the aldehyde. If this argument is based solely upon the observation that traces of ethylene oxide catalyse the decomposition of acetaldehyde, it cannot be regarded as convincing; for it is now well known that the decomposition of aldehydes is catalysed by many substances of quite different character,¹¹ some of which cannot give rise to free radicals. It is surprising that if acetaldehyde is at all formed as a major intermediate product in the decomposition of ethylene oxide, no traces of it can be detected analytically. The aldehyde must decompose instantaneously. It is very unlikely that reaction chains of appreciable length are propagated, unless they can be reflected from the vessel walls, which is most improbable. Moreover, independent series of measurements by Patat and Sachsse on the one hand,¹² and Staveley and Hinshelwood¹³ on the other, seem to indicate definitely that the free radical mechanisms developed by Rice and Herzfeld¹⁴ and others are not very relevant to many of the reactions for which they were suggested.

Comparison of the present data with the results for substituted alkylene oxides may throw additional light upon the nature of the decomposition.

Summary.

Measurements on the kinetics of the thermal decomposition of ethylene oxide vapour have been described. The products of the reaction are mainly methane and carbon monoxide. The course of the reaction can be represented approximately by a first order law, but there are certain complications. The unimolecular velocity constant falls off with decreasing initial pressure in the same manner as in other quasi-unimolecular decompositions, and the plot of k against the initial pressure has a segmented appearance. The reaction is homogeneous, and no evidence can be found of the propagation of reaction chains. The energy of activation at the higher pressures is ca. 53,000 cals, and falls slightly as the initial pressure is lowered.

The results are compared and contrasted with those previously found by Heckert and Mack; and their bearing upon other theoretical discussions of the reaction mechanism is discussed.

We should like to express gratitude to Dr. B. Lambert for his constant help in connection with apparatus, and one of us (M. M.) thanks the Rhodes Trustees for a Scholarship.

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¹¹ See *Proc. Roy. Soc., A*, 1930, **128**, 88; 1930, **128**, 82; *J.C.S.*, 1929, 1815; 1930, 2607; *Proc. Roy. Soc., A*, 1932, **135**, 23; *Faraday Soc. Trans.*, 1935, **31**, 1521, 1533.

¹² *Z. physikal. Chem., B*, 1935, **31**, 79, 105; 1936, **32**, 274, 294.

¹³ *Proc. Roy. Soc., A*, 1935, **154**, 335; *J.C.S.*, 1930, 812, 818.

¹⁴ *J. Am. C. S.*, 1934, **56**, 284.

CONDUCTOMETRIC TITRATIONS OF THE ISOMERIC CHROMIC CHLORIDES WITH SILVER NITRATE.*

BY NORMAN H. LAW.

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One of the most interesting and important applications of Werner's Co-ordination Theory concerns the constitution of the isomeric hexahydrates of the chromic chlorides, which are known in three forms, a violet (or blue), a pale green and a dark green form. Although these may be formulated on Werner's theory as $[\text{Cr}6\text{H}_2\text{O}]\text{Cl}_3$, $[\text{CrCl}, 5\text{H}_2\text{O}]\text{Cl}_2$, H_2O and $[\text{CrCl}_2, 4\text{H}_2\text{O}]\text{Cl}, 2\text{H}_2\text{O}$ respectively, the evidence in favour of the validity of these formulæ is less convincing than in other cases of such isomerism. In support of these formulæ the reaction of the chlorides in aqueous solution with silver nitrate is usually quoted but the results are not unequivocal. Thus Werner and Gubser¹ obtained from 1.152 to 1.173 equivalents of chlorine from the dark green chloride by precipitation with silver nitrate in ice-cold nitric acid solution, whereas theory requires exactly one equivalent. Moreover, Weinland and Koch² showed that the proportion of chlorine precipitated depended to a marked extent on the acidity of the solution and on the nature of the anion of the silver salt. The work of Bjerrum,³ Lamb⁴ and Lamb and Fonda⁵ established the importance of hydrolytic effects which complicate the reaction of these chlorides in solution and suggest that, if Werner's formulations are correct, the co-ordination sphere possesses an unusual degree of reactivity which is probably fundamental to such industrial arts as the chrome tanning of leather. This reactivity can readily effect the reaction with silver nitrate, especially as this is usually used in excess in analytical work. It is surprising that the less drastic method of conductometric titration has not been used hitherto.

Experimental.

The violet chloride was prepared by the method of Bjerrum (found Cr 19.51 per cent., Cl 39.92 per cent.; calc. Cr 19.52 per cent., Cl 39.93 per cent.). The pale green chloride was also prepared by the method of Bjerrum (found Cr 19.59 per cent., Cl 39.69 per cent.), and the dark green salt according to the directions of Werner and Gubser (found Cr 19.82 per cent., Cl 39.94 per cent.).

A modification of the conductivity cell designed by Robbins⁶ was used in the course of this work, it being very suitable for titrimetric work. The main feature of the cell was rigidity of the electrode supports, secured by means of a glass bar *not* immersed in the solution. The apparatus is shown

* Communicated by Dr. R. A. Robinson.

¹ Werner and Gubser, *Ber.*, 1901, **34**, 1592.

² Weinland and Koch, *Z. anorg. Chem.*, 1904, **39**, 328.

³ Bjerrum, *Z. physikal. Chem.*, 1907, **59**, 336, 581.

⁴ Lamb, *J. Amer. Chem. Soc.*, 1906, **28**, 171.

⁵ Lamb and Fonda, *ibid.*, 1921, **43**, 1154.

⁶ Robbins, *ibid.*, 1917, **39**, 646.

in Fig. 1. The titrant is delivered from a burette into the side-arm T, the major portion of the solution being in the vessel E. By means of alternate gentle suction and pressure exerted through the side-tube A, the added solution can be thoroughly mixed with the main body of liquid.

All conductivity measurements were made on solutions 0.005 *M* with respect to chromium and unless otherwise recorded the temperature was 1.5°, at which the three chlorides were comparatively stable in dilute solution; nevertheless, titrations were performed without undue delay. All conductivity measurements were corrected for dilution by multiplication by the factor (volume of original solution + added titrant)/(volume of original solution), *i.e.*, all conductivities are referred to a constant volume of solution.

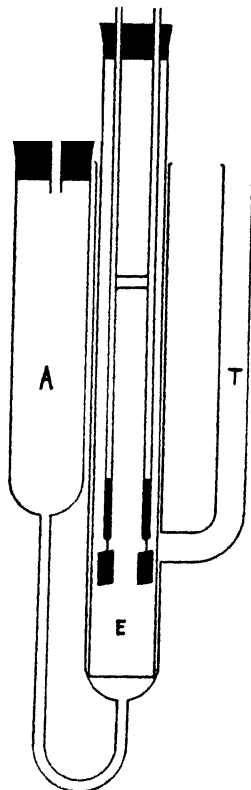


FIG. 1.—Conductivity cell for titration work (approximately $\frac{1}{4}$ natural size).

ionized chlorine and this was confirmed by gravimetric analysis of the precipitable chlorine in solutions buffered at different p_H values, the following values being obtained:

p_H	0.7	1.0	1.7	3.0	4.0
per cent. Cl pptd.	34.5	40	37	56	93

Conductometric Titrations with Silver Nitrate.—Fig. 2 shows the conductivity curves obtained at 1.5° during the titration of 0.005 *M* solutions with 0.1 *N* silver nitrate. The initial molecular conductivities were 185.8, 119.1 and 57.1 mhos. respectively. Breaks occurred corresponding to 3.0, 2.1 and 1.54 equivalents of chlorine and in each case the ascending part of the curve after the break always corresponded to the calculated curve for an excess of silver nitrate. The superiority of conductometric titration over gravimetric analysis of the precipitable chlorine can be seen from the fact that from the pale green salt, nearly all the chlorine was precipitated by the addition of a bulk amount of reagent in

Experimental Results.

Van't Hoff Factor.—Cryoscopic determinations using 0.05 *M* solutions gave a Van't Hoff Factor of 3.40, 2.73 and 1.95 for the violet, pale green and dark green salts respectively. The isopiestic vapour pressure method⁷ applied to the violet salt gave 3.89 in 0.3 *M* solution and 3.75 in 0.6 *M* solution.

Quantitative Precipitations with Silver Nitrate.—By boiling any of these chlorides with silver nitrate solution in the presence of nitric acid three equivalents of chlorine are precipitated. From an acid-free, ice-cold solution of the pale green chloride silver nitrate precipitates 85 per cent. of the total chlorine, the remaining 15 per cent. being precipitated on warming with a little nitric acid. Direct precipitation from ice-cold solution of the dark green chloride gave 88 and 90 per cent. of the total chloride in acid-free solution, and 34 and 40 per cent. in dilute nitric acid solution. These figures, combined with the observation of Weinland and Koch that the nature of the anion of the silver salt had a profound influence on the amount of chlorine precipitable led us to suspect that the p_H value of the solution was an important factor in determining the amount of

⁷ Robinson and Sinclair, *J. Amer. Chem. Soc.*, 1934, 56, 1830.

excess, whilst the more cautious addition of silver nitrate during conductometric titration gave a break at a point only slightly beyond the theoretical.

A similar titration of the violet salt was carried out at 25°, the initial molecular conductivity of 359 mhos. falling linearly to 354 mhos. when 3 equivalents of silver nitrate had been added, when a sharp break occurred and the conductivity rose at the rate calculated for excess of silver nitrate.

Since conductometric analysis was found to be superior to direct gravimetric analysis in the case of the pale green salt, the precipitations

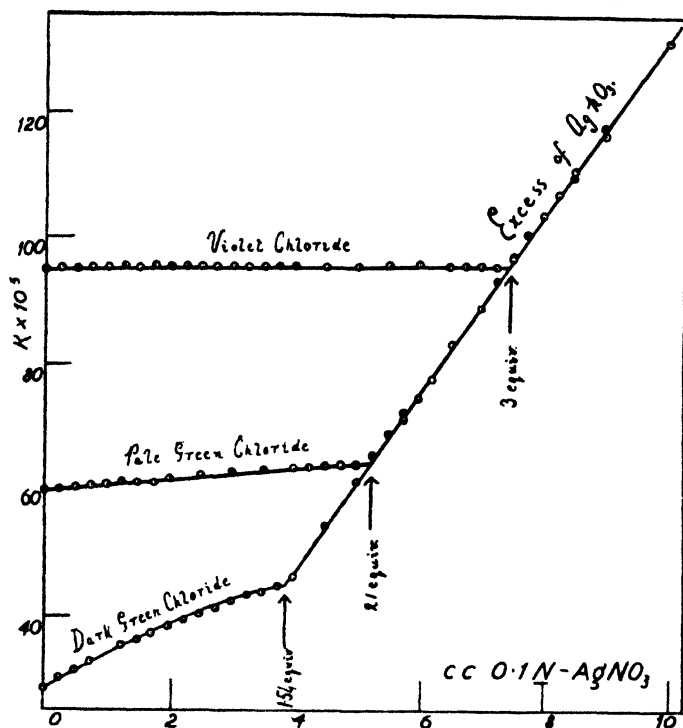


FIG. 2.—Conductometric titration of 50 c.c. of 0.005 *M* chromium chlorides with 0.1 *N*— AgNO_3 .

from solutions of the dark green salt in buffered solutions were repeated, with conductometric analysis. Fig. 3 gives the curves obtained for seven such solutions as follows:

p_{H}	Buffer.	End point.
2.3	Solution + nitric acid	1.00 equiv.
3.0	" " "	1.00
3.6	Citric acid — Na_2HPO_4	1.05
4.0	" " "	1.11
4.3	" " "	1.20
4.6	" " "	1.24
5.0	Citric acid — Sodium citrate	2.0

Separate experiments showed that the buffer solutions did not precipitate a silver salt. In Fig. 3 the scale of the ordinate on the graph has been adjusted in each case, so that each curve starts at the same initial value. These curves are very significant. A few experiments were carried out with buffered solutions of the other two chlorides. The end-points for the violet salt do not appear to be influenced by the p_{H} of the solution,

titrations at p_H 3 and 5 giving curves of the same type as that for the violet chloride in Fig. 2. This was also true of the pale green salt at p_H 3, but at p_H 4, although a break was found at 2 equivalents, the slope of the curve

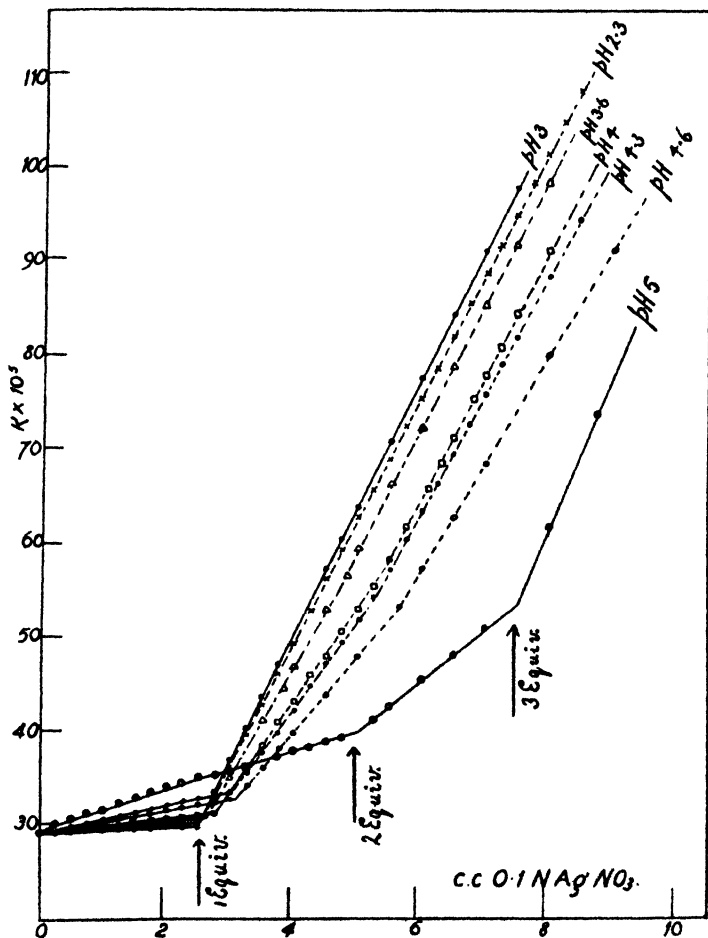


FIG. 3.—Conductometric titration of $0.005 M-[CrCl_3 \cdot 4H_2O]Cl$ with $0.1 N-AgNO_3$ in buffered solutions.

on further addition of silver nitrate was less than the theoretical, showing that slight precipitation was still in progress. This was more marked at p_H 5 in which case a second break was found at 3 equivalents, the form of the curve being similar to that for the dark green salt at p_H 5 shown in Fig. 3.

Discussion.

For all three salts both the Van't Hoff Factor and the molecular conductivity support the formulations accorded on Werner's theory. That the violet salt dissociates into three chloride ions is also shown by the fact that it always gives three precipitable chlorine atoms and the curve in Fig. 2 shows that there is no discontinuity in the curve such as might be expected if precipitation occurred in stages. Moreover, the amount of chlorine precipitated is independent of the p_H value of the solution, at least between p_H 3 and 5. The replacement of chloride ions

by nitrate ions proceeds with little change in conductivity, consistent with the very similar mobilities of these two ions. There seems, therefore, to be no doubt as to the constitution of this chloride.

In the case of the pale green salt, the conductometric curve in Fig. 2 shows that the salt has two ionised chlorine atoms, but a slight attack on the third co-ordinated chlorine atom occurs during precipitation witnessed by the break at 2.1 equivalents and the slight increase in conductivity during precipitation. This must be accounted for by any adequate theory, as well as the fact that the reactivity of this third chlorine atom is favoured at high p_H values and repressed at low p_H values.

The dark green chloride in aqueous solution gives an anomalous conductivity curve with a break at 1.54 equivalents, together with a considerable increase in conductivity during precipitation, showing that the co-ordinated chlorine atoms are much more loosely bound. In acid solution, however, the salt behaves as a uniunivalent electrolyte, the co-ordination sphere being more readily attacked as the p_H value increases. At the same time the curve for excess of silver nitrate departs more and more from the theoretical value and a second break appears in the vicinity of 2 equivalents. At p_H 5 the first break has been smoothed out and another appears at 3 equivalents, but it should be noted that the conductivity at this point does not correspond to a trivalent salt; rather is it characteristic of a bivalent salt. As the p_H of the unbuffered solution is 4.75, the break at 1.54 equivalents in Fig. 2 cannot be given especial significance. Of greater importance is the fact, that, provided the p_H value of the solution is suitably adjusted, the formal proof of the constitution of these salts is complete.

Nevertheless, there remains much to be explained, particularly the progressive attack of the second chlorine atom of the dark green chloride as precipitation proceeds in an unbuffered solution and the increasing reactivity of this atom as the acidity is decreased together with the reactivity of the third chlorine atom at high p_H values. These reactions must depend on a most complex series of hydrolytic reactions, in which substitution of either hydroxyl ions or water molecules within the co-ordination sphere can occur and it does not seem wise to attempt any further explanation until more knowledge of these hydrolytic reactions is available.

Summary.

Conductivity titrations of the reaction between silver nitrate and each of the three isomeric chromic chlorides are described and it is shown that a conductometric investigation is superior to a direct gravimetric analysis of precipitable chlorine.

The violet chloride undoubtedly yields three ionised chlorine atoms and the pale green two chlorine atoms, except in solutions of p_H value in the vicinity of 5 when the third atom is easily precipitated.

The dark green salt is much more reactive. A formal proof of its constitution results from work in very acid solution, but as the p_H is increased the second and, at high p_H values, the third chlorine atom becomes precipitable.

The author wishes to offer his sincere thanks to Dr. R. A. Robinson for his advice and encouragement in the course of this investigation.

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THE PHOTOCHEMISTRY OF NITRATES, NITRITES AND NITRO-COMPOUNDS. II.

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We have recently undertaken a systematic study of the photochemistry of nitrates, nitrites and nitro-compounds. The ultraviolet absorption spectra of some of these compounds have previously been described.¹ Melvin and Wulf have simultaneously reported spectral measurements from which they have attempted to attribute a banded absorption in the near ultraviolet in mixtures of nitric oxide, nitrogen peroxide and water vapour to the carrier molecule HONO.² The data previously given by us substantiate the argument of Melvin and Wulf strongly, and interesting conclusions can be drawn from a comparison of the two sets of data. In the present paper these conclusions are outlined, and further spectral measurements for other related compounds are given. The qualitative course of the photochemical decomposition of nitrites is also discussed.

Experimental Details.

The instruments used in measuring the absorption spectra were as previously described. In addition, some visual measurements were made with a small constant deviation glass spectroscope.

The photochemical changes were followed by a method essentially the same as described by Thompson and Linnett.³ The radiation from a mercury lamp was condensed by passing through a transparent quartz spherical flask containing either water or a solution filter, and then directed upon the reaction cell. Pressure changes were followed manometrically. In some experiments the reaction vessel was enclosed within a water thermostat having a large quartz window at the side.

Methyl, ethyl and *iso*-amyl nitrites were prepared as before. Secondary butyl nitrite

$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}(\text{CH}_3) \cdot \text{O} \cdot \text{NO}$ was obtained by the action of nitrous acid upon secondary butyl alcohol. The nitrite layer, which is insoluble in water, was separated, dried and purified by fractional distillation *in vacuo*.

Nitroso-chloro-propane $\text{CH}_3 \cdot \text{CH}(\text{NO}) \cdot \text{Cl}$ was prepared by the method of Ponzio⁴ by leading a stream of chlorine over a solution of acetoxime in 10 per cent. caustic soda solution. The chloro derivative separated as a dark blue liquid which was dried over calcium chloride and subsequently fractionated *in vacuo*. It was stored over ice since it is liable to decompose at room temperatures.

N-methyl O-methyl hydroxylamine $\text{CH}_3 \cdot \text{N}(\text{OCH}_3) \cdot \text{OH}$ was prepared by the method of Jones.⁵ N-methyl N-methoxy urethane was first prepared by

¹ *Far. Soc. Trans.*, 1936, **32**, 674.

² *J. Chem. Physics*, 1935, **3**, 755.

³ *J. Chem. Soc.*, 1935, 1452.

⁴ *Chem. Zentralblatt*, 1906, **10**, (1), 1692.

⁵ *Am. Chem. J.*, 1898, **20**, 43.

the methylation of hydroxy-urethane, the latter being formed from the interaction of hydroxylamine and chloroformic ester. The product was then heated in a sealed tube with concentrated hydrochloric acid, and distilled with potash to liberate the free base, which was purified by fractional distillation *in vacuo*.

Dimethyl nitrosamine was prepared by the method of Renouf⁶ and diethyl nitrosamine by that of Geuther.⁷ Both methods depend essentially upon the action of nitrous acid upon a secondary amine.

Results.

(1) Spectral Data.

In Part I the ultraviolet absorption spectra of methyl nitrite, methyl nitrate and nitro-methane and the corresponding ethyl derivatives, were described. As then explained, the nitrites show a system of diffuse bands in the near ultraviolet; the intensity distribution within individual bands of the system is peculiar, and moreover different from one band to another. In view of the considerations of the nitrous acid spectrum given below, it became desirable to attempt to measure with as great an accuracy as possible the wavelength of the "origin" of each band. The nature of the band obviously makes such a measurement difficult, but the values previously given for the "centres" of the bands have now been revised, and the corrected values are given below.

(i) *Methyl Nitrite*.—The spectrum is represented diagrammatically in Fig. 1 (a), the wave-numbers of the bands being given.

(ii) *Ethyl Nitrite*.—Fig. 1 (b) similarly shows the system of bands observed. As with methyl nitrite, the most intense bands have no marked head, and two broad bands are noticed at the long-wavelength end of the system; these two bands appear at first sight to be distinct from the remainder of the system.

(iii) *Iso-amyl nitrite*.—The absorption of the vapour of this substance is very similar to that of both methyl and ethyl nitrites. The band system in the near ultraviolet is shown in Fig. 1 (d). Each band is diffuse and there is not definite degrading in either direction. The two longest wavelength bands have not, however, the abnormally broad nature of those of methyl and ethyl nitrites just referred to.

(iv) *Sec-butyl nitrite*.—As with the above compounds, there is a system of diffuse bands between 4000-3000 Å. and a continuous absorption at shorter wavelengths. At higher pressures the continuum extends to longer wavelengths and eventually overlaps the bands system. The latter is shown diagrammatically in Fig. 1 (c). The striking difference between this system of bands and each of the above is that each of the bands of butyl nitrite degrades to the red and has a distinct head on the short-wavelength side.

(v) *Dimethyl nitrosamine*.—The ultraviolet absorption is very similar to that of the nitrites. Between 3900-3200 Å. is a system of diffuse bands with no marked head, and at shorter wavelengths a region of continuous absorption which extends to longer wavelengths as the pressure is increased. The approximate wavelengths of the "centres" of the most intense bands are 3768, 3645, 3522, and 3305 Å.

(vi) *Diethyl nitrosamine*.—The spectrum is similar to that of dimethyl nitrosamine, except that the narrow region of absorption between 4000-3200 Å. has not been clearly resolved into bands.

(vii) *N-methyl O-methyl hydroxylamine*.—There is continuous absorption from about 2500 Å. to shorter wavelengths.

(viii) *Nitrosochloropropane*.—This compound, which is deep blue in colour in the liquid state has a region of absorption in the red about 7500-5260 Å., and a second region of continuous absorption at wavelengths

⁶ *Ber.*, 1880, 13, 2170.

⁷ *Ann.*, 1863, 128, 151.

shorter than about 2400 Å. The first region has not been resolved into bands, but the dispersion used was small.

(2) Photochemical Data.

(a) *Methyl nitrite*.—When the vapour of this substance is irradiated with the unfiltered light of a mercury vapour lamp, a decrease in pressure

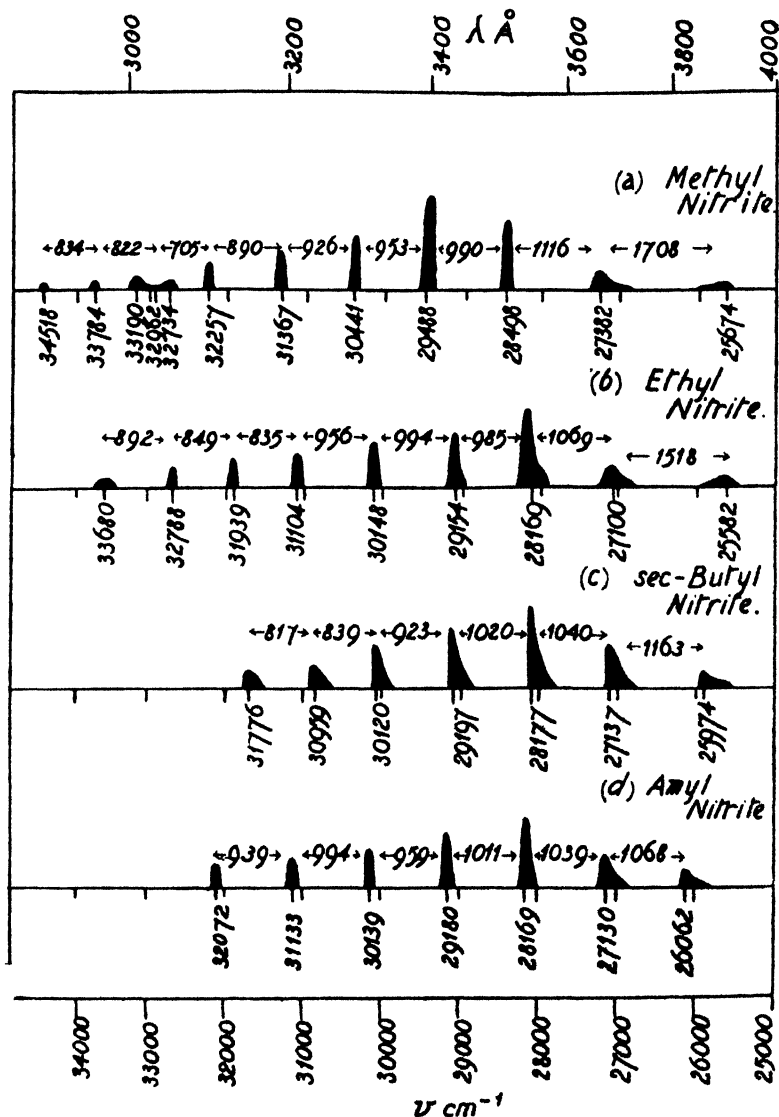


FIG. 1.

occurs. The decrease is at first linear with time, but falls off in the later stages. When the reaction is apparently complete, as indicated by no further pressure change, the decrease is about 37 per cent. of the initial pressure. (An appreciable dead-space error has not been allowed for.) Table I summarises a typical run.

At the beginning of a run there was usually a pressure increase of a few millimetres suggesting a slight induction period, but this may have been due to a minor heating effect. Preliminary drying with phosphorus pentoxide did not affect the general course of a run.

During the progress of a run a white solid was deposited on the back face and sides of the cell, but with the reaction cell in air none was deposited on the front face. This observation may be significant, and is discussed below.

The solid deposit was first examined. It was insoluble in water, but dissolved in concentrated nitric acid. A suspension in water was examined by Schryver's test for formaldehyde. The magenta colour produced suggested that the solid contained paraformaldehyde. The following sensitive reaction confirmed this result. A sample of the solid was warmed with concentrated sulphuric acid, and a rod previously dipped in benzene was held in the vapours. A deep red colour was produced.

The solid deposit had an unpleasant smell and since the aqueous washings of the reaction cell were acidic, formic acid was indicated. A solution of silver nitrate was gradually darkened and silver deposited by the aqueous extract, which supports this conclusion.

The gaseous products were withdrawn into a gas-holder over mercury. Apart from a small amount of unchanged methyl nitrite, possible constituents might be carbon monoxide, hydrogen, nitrogen, nitrous oxide, nitric oxide, carbon dioxide, and oxygen. The accurate analysis of such a mixture is very difficult. Several procedures were adopted. In the first, the gas mixture was separated into two fractions, (i) condensable in liquid air, (ii) not condensable by liquid air. Table II shows the results of six analyses, each sample being taken from an independent run.

TABLE I.—INITIAL PRESSURE
435 mm.

<i>t</i> (mins.)	pressure decrease mm.
20	1
80	14
137	24
228	42.5
343	66
449	85.5
530	100
	light off
1416	108
	light on
1514	119
1620	128
1762	140
1838	145
1902	149
1972	150
2200	157
2600	162
2899	165
2941	165

TABLE II.

Run No.	1	2	3	4	5	6	Mean.
Percentage condensed	49.5	50.1	50.2	45.2	49.8	56.1	50.1
Percentage not condensed	50.5	49.9	49.8	54.8	50.2	43.9	49.9

It is seen that the proportions of condensable and non-condensable products are roughly equal.

The non-condensable fraction might be expected to contain nitrogen, oxygen, carbon monoxide, and hydrogen. Absorption with alkaline pyrogallol ammoniacal cuprous chloride, and subsequent combustion showed that carbon monoxide were present only in small amount (about 5 per cent. of the total fraction) and oxygen only in traces. The bulk of the non-condensable fraction appeared to consist of nitrogen.

The condensable fraction was slowly but almost completely dissolved in water, which suggested the presence of considerable quantities of nitrous oxide. This was confirmed by a very rapid absorption of about 90 per cent. of the gas by absolute alcohol. The residue contained a small amount of combustible gas, but its exact nature could not be ascertained. The

residue also contained traces of nitric oxide, which turned saturated ferrous sulphate brownish.

It is therefore concluded that the gaseous products in the photo-decomposition of methyl nitrite vapour contain about 45 per cent. nitrogen, 45 per cent. nitrous oxide, small amounts of carbon monoxide and hydrogen and traces of other gases.

(b) *Ethyl nitrite*.—On illumination of gaseous ethyl nitrite with the full radiation of a mercury lamp, there is a pressure decrease which follows the same general course as with the methyl nitrite above, but this decrease is only about 30 per cent. of the initial pressure, *i.e.* smaller than with the latter substance. With ethyl nitrite therefore there is produced either less solid vapourless product, or more gaseous products, than with methyl nitrite.

Drops of a faintly yellow liquid remained in the cell at the end of a run. This liquid was acidic, and when tested with Schiff's reagent for the presence of aldehydes it gave a positive result.

The gaseous products were withdrawn and analysed as before in the case

TABLE III.

Run No.	1	2	3	Mean.
Percentage condensed	35.3	40.6	40.4	38.8
Percentage not condensed	64.7	59.4	59.6	61.2

of methyl nitrite. For three runs the runs shown in Table III were obtained.

Thus the proportion of non-condensable gases is greater than with methyl nitrite.

The condensable fraction was nearly completely soluble in alcohol, leaving a small combustible residue which appeared to be primarily methane. The non-condensable fraction contained some carbon monoxide and a little methane but was mainly nitrogen. The total percentage composition of the gaseous products for three typical runs is given in the following table:—

TABLE IV.

	Run 1.	Run 2.	Run 3.	Mean.
Nitrogen percentage	39.3	37.6	38.3	38.4
Nitrous oxide percentage	25.7	32.1	32.9	30.2
Carbon monoxide percentage	22.2	17.0	15.3	18.1
Methane, etc., percentage	12.8	13.3	13.5	13.2

It is seen that the principal constituents are again nitrous oxide and nitrogen, but these are not present in exactly equivalent proportions. The ratio of carbon monoxide to "methane" is also not unity. An interpretation of these facts is suggested below.

Discussion.

From a spectroscopic standpoint the most interesting considerations relate to the system of bands shown by the nitrites in the near ultra-violet. From a comparison of the nitrites with nitrates and nitro-compounds it was previously suggested that this band system was shown exclusively by compounds containing the —N=O group. The present work supports this conclusion (*e.g.* the bands are absent with the substituted hydroxylamine). In Fig. 1 the positions of the nitrite bands

for the different compounds are shown. The bands of dimethyl nitrosamine, which are somewhat more difficult to measure, lie at closely similar wavelengths.

The above conclusion can, however, be taken further: the tertiary nitroso-compound, nitroso-chloropropane, does not give a corresponding absorption in the same near ultraviolet region. It thus appears that the system of bands between 3000-4000 Å. is characteristic of compounds in which the —N=O group is attached to an atom having free electrons, as in —O—N=O , or >N—N=O . The possibility of resonance in such

structures, which may be representable by $\text{—}\overset{\text{O}}{\underset{|}{\text{O}}}\text{—}\overset{\text{N}}{\overset{\curvearrowright}{\text{N}}}=\overset{\text{O}}{\text{O}}$ and $\text{>}\overset{\text{N}}{\overset{\curvearrowright}{\text{N}}}\text{—}\overset{\text{N}}{\overset{\curvearrowright}{\text{N}}}=\overset{\text{O}}{\text{O}}$,

may have some bearing upon this. If the level of the tertiary nitroso-compound at about 6500 Å. corresponds to the near-ultraviolet level of the nitrites, but is displaced in the latter substances as a result of resonance phenomena, we might take the difference in energy between the level in the two cases as representing the resonance energy of the —O—N=O structure. This will be roughly $3700 \text{ Å.} - 6500 \text{ Å.} \equiv (27,000 - 15,400) \text{ cm.}^{-1} = 11,600 \text{ cm.}^{-1} \equiv 1.44 \text{ volt} \equiv 33 \text{ kcal. per gm. mol.}$ On this hypothesis the difference between the lowest level of the tertiary nitroso-compounds on the one hand, and the nitro-compounds on the other, may represent the resonance energy of the nitro-group. This will be roughly $(40,000 - 15,400) = 24,600 \text{ cm.}^{-1} \equiv 70 \text{ kcal. per gm. mol.}$ Some doubt, however, is cast upon this interpretation, since the difference in energy between the lowest levels of the nitrites and nitrates, which might also perhaps be associated with resonance in the nitro-group, is only 37 kcal.; but the complex nature of the nitrate structure may be the reason for the discrepancy.

It is clear that in all the nitrites the main vibration frequency excited in the band region is about 1000 cm.^{-1} , decreasing noticeably to higher levels. Comparison with known valency vibrations of similar compounds containing atoms of similar mass, shows that it is reasonable to assign the frequency 1000 to a valency vibration in the nitrite molecule.*

It is interesting to correlate the above data with those of Melvin and Wulf for nitrous acid. The excited level of this compound agrees well with those of the alkyl nitrites. The frequency interval between the more intense bands (ca 1000 cm.^{-1}) implies too that this frequency involves the same vibration as is excited in the alkyl nitrites. The interpretation of the feebler bands of nitrous acid is less obvious. Of many possible hypotheses, two appear most probable, each differing from that suggested by Melvin and Wulf. These are best explained with the help of Fig. 2.

According to Fig. 2 (a) the satellite bands are interpreted as being due to vibration levels superposed upon the main vibration levels. The magnitude of the superposed vibration is about 250 cm.^{-1} , and of the order of a deformation oscillation. It may be reasonable to suppose that with the molecule H—O—N=O such a deformation is more excitable by virtue of the nature of the light H atom, whereas with the heavier alkyl radicals this is impossible. On the other hand, there seems to be no reason why deformation vibrations should not be excited above the two

* For example, the frequencies of the molecule $\text{N} \equiv \text{N} = \text{O}$ are given as 2224, 1285 and 589; of $\text{Cl—C} \equiv \text{N}$ as 729, 2201 and 397; and of $\text{Cl—N} = \text{O}$ as 923, 1832 and 633.

lowermost excited vibration levels. Also the value 250 cm^{-1} is perhaps rather lower than might have been expected for the deformation oscillation frequency.

The alternative hypothesis involves the assumption that two vibration levels are excited, one about 1000 cm^{-1} , the other about 2250 cm^{-1} . The satellite bands are thus interpreted as combinations of the two normal frequencies (Fig. 2 (b)).

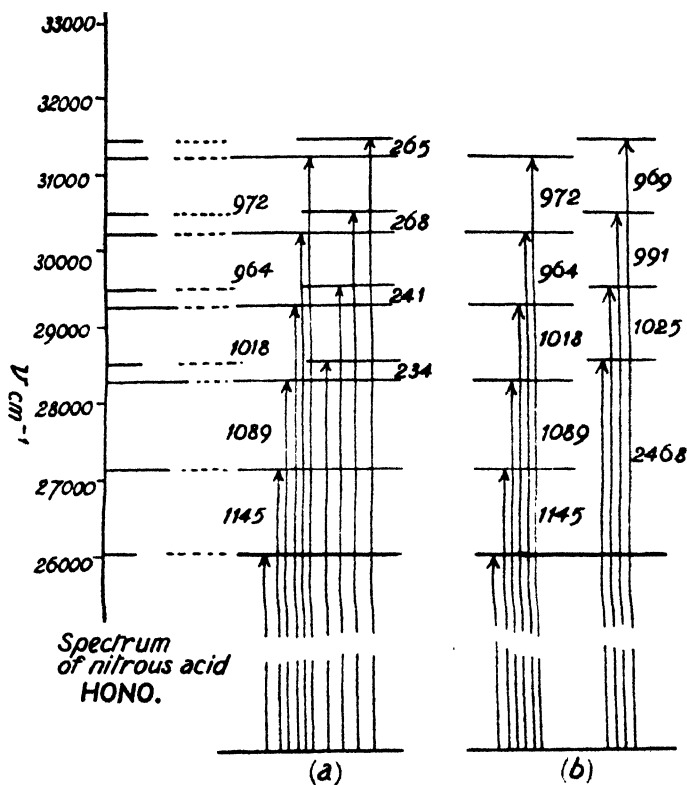
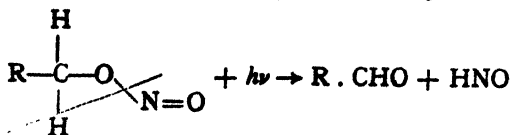
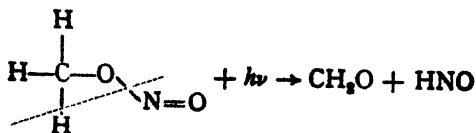


FIG. 2.

The spectroscopic data suggest that the primary act in absorption of ultraviolet frequencies by the nitrites is a dissociation process, since the bands are diffuse under high dispersion. The analytical results suggest that the primary process is represented in general by :



e.g. for methyl nitrite,



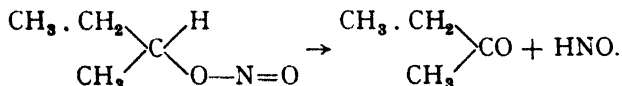
The subsequent changes are somewhat different for the different nitrites, but, in general, decomposition of the hyponitrous acid leads to much nitrogen and nitrous oxide.

With methyl nitrite the formaldehyde first formed polymerises thermally or photochemically to give solid paraformaldehyde. Carruthers and Norrish⁸ have studied the photochemical polymerisation of formaldehyde and shown that it is catalysed by traces of formic acid, the solid polymer being deposited preferentially on a cold surface. As explained above, traces of formic acid were detected among the end-products. This might well arise from an oxidation of a little formaldehyde by the decomposition products of the hyponitrous acid. These facts taken together suggest why the deposition of the polymer occurs only on the back face of the cell unless the latter is cooled uniformly.*

The traces of carbon monoxide and hydrogen found among the decomposition products of methyl nitrite presumably arise from a photochemical decomposition of formaldehyde.

With ethyl nitrite we should expect the primary products to be acetaldehyde and hyponitrous acid. Photo-polymerisation of acetaldehyde does not occur as easily as with formaldehyde, and is not catalysed in the presence of acetic acid. We might therefore expect to obtain a much smaller pressure decrease in the run than with methyl nitrite. Actually the decrease in pressure is smaller, though not markedly. It seems probable that some of the acetaldehyde is decomposed giving methane and carbon monoxide, and some is oxidised by the decomposing HNO to give the drops of liquid acetic acid, which in turn dissolve some acetaldehyde. The part played by the HNO in oxidising the aldehyde may be more significant here than in the case of methyl nitrite, and lead to a ratio nitrogen : nitrous oxide appreciably different from unity.

The above mechanism agrees with that suggested by Anderson, Crumpler and Hammick for the photolysis of more complicated organic nitroso compounds.⁹ It should be possible to test the hypothesis by a consideration of other examples, *e.g.* *iso*-amyl nitrite,



Such work is now in progress. Preliminary experiments show that on illumination of this substance with the light of the mercury lamp, an increase of pressure is observed, which can be reconciled with the mechanism suggested for the decomposition.

* *Far. Soc. Trans.*, 1936, 32, 195.

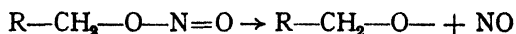
* A microanalysis of the solid polymerised product gave C 38.19 per cent., H 6.84 per cent., O 54.97 per cent. This corresponds to the empirical formula $\text{C}_{2.103}\text{H}_{0.700}\text{O}_{2.437}$. Assuming the non-branching mechanism of Norrish and Carruthers the formula of the product should be $\text{C}_{n+3}\text{H}_{n+4}\text{O}_{n+3}$, n being the chain length for the photopolymerisation of formaldehyde in the presence of formic acid. It is likely that the water formed in the final chain-breaking link will be occluded in the solid product. We could then correct the formula of the latter to $\text{C}_{2.103}\text{H}_{0.770}\text{O}_{2.103}$. Then

$$\frac{2n+4}{n+3} = \frac{6.276}{3.182} \text{ whence } n = 68.$$

It may, however, be unwise to attach too much significance to this calculation since small errors in the microanalytical work may considerably affect the value of n obtained.

⁹ *J. Chem. Soc.*, 1935, 1679.

If the mechanism now suggested for the photo-decomposition of the nitrites is correct, it is interesting to contrast it with that which has been suggested as the primary stage in the thermal decomposition of these substances, namely, according to Steacie and his collaborators,



Summary.

Previous measurements on the photochemistry and spectroscopy of nitrates, nitrites and nitro compounds have been extended. A comparison is made with the data for nitrous acid recently reported by other workers, and interpretations are suggested to explain the structure of the regions of banded absorption in the nitrite spectra. The products of photochemical decomposition of the nitrites are described, and a mechanism is suggested to represent in general the course of this reaction.

We are grateful to the Government Grant Committee of the Royal Society for assistance in the purchase of instruments.

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FREE AND TOTAL SURFACE ENERGIES AND RELATED QUANTITIES.

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The object of the present investigations is primarily to compute the values of the free and total surface energies of super-cooled liquids at the absolute zero, and to discuss their dependence on constitution and their relation to other physical constants. In the examination of the literature it became evident that large gaps existed in our knowledge of other surface tension constants and it is a second object of this paper to fill in these gaps where possible. It should be emphasised at the outset that the possibility of obtaining figures for surface energies depends on the existence of reliable data giving the surface tensions of pure liquids at different temperatures.

These data, in all instances, form the *terminus a quo*, and it is not till one makes a search into the literature that one realises how scanty are the relevant data. There are determinations in plenty of the surface tensions of isolated substances, at one or two not very widely separated temperatures. What is needed, however, for the purposes of such investigations as this, is a set of tables which shall give the surface tensions over a wide range of temperature, of different series of related organic compounds—esters, ethers, ketones and the like—where special attention has been paid to the purification of the specimens and to the trustworthiness of the surface tension method. It is hoped that one or two of these gaps will be filled in the near future.

Taking, however, the published figures as they stand, and selecting

therefrom what appear to be the most accurate results, the authors have calculated the following constants for the different substances listed :

(i) The value of the constant γ_0 and the exponent n in the power law connecting surface tension and temperature

$$\gamma = \gamma_0(1 - m)^n$$

(m here stands for reduced absolute temperature and γ_0 is the surface tension of the super-cooled liquid at the absolute zero).

(ii) The value of the exponent p in a generalised form of Macleod's equation

$$\gamma = C(\rho_L - \rho_V)^p$$

(iii) The value of E_0 (or e_0) the total or the free molecular surface energy of the super-cooled liquid at the absolute zero.

Having obtained these quantities it becomes possible to investigate their dependence on chemical constitution and their relation to other physical constants of the liquid. The present paper is concerned chiefly with the listing of these data—only a tentative discussion is given of the related matters.

The figures of primary importance are those for *surface tension and temperature*. These data being critically selected, either or both of two methods may be followed. The critical temperature being known, a logarithmic plot of $(1 - m)$ and γ suffices to determine the required constants γ_0 and n . Or the equation may be attacked by the method of least squares (or some related method), labour being reduced by employing mechanical aids to computation.¹ We have found it convenient to follow both these methods. The graphical method, though less precise, indicates very clearly to the eye whether the power law is or is not closely followed.

It should be noted that, even if the critical data are not available, it is possible, without much difficulty to evaluate b , γ_0 and n in the equation

$$\gamma = \gamma_0(1 - b\theta)^n$$

where b is the reciprocal of the critical temperature. Thus, if, by interpolation methods, $d\gamma/d\theta$ is found for different values of θ , the quantity $\gamma \cdot d\theta/d\gamma$ is linear in θ , and a plot of these two variables determines n and b . The value of γ_0 may then be obtained from the original equation.

The values of γ_0 and n having been determined it becomes possible to calculate the total energy (λ), which is given by

$$\lambda = \gamma - m \cdot \frac{\partial \gamma}{\partial m} = \gamma_0(1 - m)^{n-1} \cdot \{1 + m(n - 1)\},$$

so that values showing the magnitude of λ at any required temperature may be obtained from the values of γ_0 and n listed in this paper.

The parachor P , is usually defined as the value of $M \cdot \gamma^{1/3}/(\rho_L - \rho_V)$. This definition is convenient, inasmuch as the parachor may then be obtained from one determination of a surface tension and a density—the expression just given being, of course, independent of the temperature if Macleod's law is followed. Actually many unassociated substances follow a generalised form of Macleod's law in which

$$\gamma = C(\rho_L - \rho_V)^p$$

¹ In our calculations, the work was considerably expedited by the use of a "Nova Brunsviga" calculating machine.

and p which is constant for any one liquid varies from liquid to liquid, and is, in many instances, sensibly different from 4. The assumption of the "fourth power law," leads in these instances to values of the parachor which show a sensible drift with temperature—a drift which disappears when the appropriate value of p is chosen, and the parachor P computed from

$$P = M \cdot \gamma^{1/p} / (\rho_L - \rho_V) = MC^{1/p}$$

where C is the constant of Macleod's equation in its general form.

If, following Katayama, we define the free molecular surface energy (e) as $\gamma \cdot \frac{M^{\frac{1}{2}}}{(\rho_L - \rho_V)^{\frac{1}{2}}}$, instead of $\gamma \cdot \frac{M^{\frac{1}{2}}}{\rho_L^{\frac{1}{2}}}$, with a similar expression for the total molecular surface energy (E) in which λ replaces γ , it is not difficult to arrive at expressions which give, very accurately, the march of these quantities with temperature.

It is convenient to take the equations

$$\gamma = \gamma_0(1 - m)^n \text{ and } \gamma = C(\rho_L - \rho_V)^p$$

as fundamental. They are the simplest expressions connecting the fundamental quantities surface tension, density and temperature, they are easily tested graphically or algebraically, and the constants γ_0 , C , n and p are readily and accurately calculable. In terms of these constants we at once find

$$e = \gamma \cdot \frac{M^{\frac{1}{2}}}{(\rho_L - \rho_V)^{\frac{1}{2}}} = e_0 \cdot (1 - m)^{n - \frac{2n}{3p}}$$

where

$$e_0 = \gamma_0^{1 - \frac{2}{3p}} \cdot (MC^{1/p})^{\frac{1}{2}} = \gamma_0^{1 - \frac{2}{3p}} P^{\frac{1}{2}},$$

where P is the parachor.

Similarly,

$$E = \frac{\lambda M^{\frac{1}{2}}}{(\rho_L - \rho_V)^{\frac{1}{2}}} = E_0(1 - m)^{(n - \frac{2n}{3p} - 1)} \{1 + m(n - 1)\},$$

where $E_0 = \gamma_0^{1 - \frac{2}{3p}} P^{\frac{1}{2}}$, and we see, therefore, that $E_0 = e_0$.

As the figures will show, n does not vary greatly from liquid to liquid, and for rough computations may be assumed to be constant at the value 1.2. If in addition we assume, as in the ordinary parachor calculations that $p = 4$, we find—

$$e = e_0(1 - m) \text{ and } E = E_0\{1 + 0.2m\},$$

as was pointed out by Katayama. It would seem, then, that the curves between these quantities and the temperature are rectilinear, starting from the same point at the absolute zero, e diminishes to zero at the critical temperature, while E increases to a maximum at the critical temperature. This does not seem plausible, and the fact is that for practically all the substances which we have examined, the index $(n - \frac{2n}{3p})$

is a little greater than unity, so that $(n - \frac{2n}{3p} - 1)$ is a little greater than zero. The effect of the power term in the expression for E , insignificant at low temperatures, shows its importance in the neighbourhood of the critical point by pulling the curve down to the zero level.

TABLE I.

Substance.	Authority.	γ_0 .	n .	p .	ϵ_0 .
Methyl formate . . .	R. and S.	75.51	1.218	4.00	980
" " *	R. and S.*	76.90	1.216	3.976	995
" " "	<i>I.C.T.</i>	77.80	1.230	3.99	1005
Methyl acetate . . .	<i>I.C.T.</i>	69.66	1.2044	4.019	1084
" " "	R. and A.	67.26	1.20	3.97	1060
Methyl propionate . .	R. and A.	64.60	1.217	4.03	1169
" " "	<i>I.C.T.</i>	65.50	1.205	3.97	1170
Methyl butyrate . . .	<i>I.C.T.</i>	63.10	1.232	4.05	1270
" " "	R. and A.	63.10	1.234	4.00	1270
Ethyl formate . . .	R. and A.	67.30	1.234	3.90	1045
" " "	<i>I.C.T.</i>	67.70	1.218	3.89	1054
Ethyl acetate . . .	R. and S.	63.92	1.215	4.03	1149
" " "	<i>I.C.T.</i>	66.90	1.232	4.00	1190
Ethyl propionate . .	H., R. and L.	59.34	1.162	3.70	1237
" " "	R. and A.	60.30	1.21	3.93	1214
Propyl formate . . .	R. and A.	62.69	1.213	4.01	1154
Propyl acetate . . .	R. and A.	59.75	1.210	3.95	1240
n Butyl acetate . . .	Wa. and S.	58.75	1.222	3.99	1317
Ethane . . .	M. and W.	46.06	1.15	3.846	596
Propane . . .	M. and W.	57.45	1.356	4.4	763
n Butane . . .	C. and M.	52.67	1.241	4.542	924
Isopentane . . .	H., R. and L.	51.29	1.217	4.193	1009
Hexane . . .	H., R. and L.	51.74	1.200	4.07	1126
" " "	Schiff.	53.41	1.233	4.014	1160
Octane . . .	R., S. and C.	53.60	1.243	3.937	1373
" " "	H., R. and L.	53.83	1.252	4.085	1384
Decane . . .	H., R. and L.	54.95	1.251	3.834	1596
n Hexacosane . . .	Sch. and K.	—	—	3.79	2926
n Dotriacontane . . .	H. and M.	—	—	3.55	3498
n Hexacontane . . .	Sch. and K.	—	—	5.56	4819
Acetylene . . .	M. and W.	62.12	1.213	3.985	621
Ethylene . . .	M. and W.	53.78	1.295	4.19	600
Propylene . . .	M. and W.	54.80	1.233	4.014	756
Allylene . . .	M. and W.	61.16	1.260	4.062	764
Benzene . . .	R. and S.	69.18	1.239	3.83	1180
" " *	R. and S.*	72.11	1.23	3.97	1232
" " "	H., R. and L.	71.60	1.229	3.86	1216
" " "	<i>I.C.T.</i>	76.29	1.223	3.82	1210
" " "	Sugden.	70.26	1.205	3.91	1202
Toluene . . .	H., R. and L.	65.72	1.226	3.79	1271
" " *	W. and S.*	66.91	1.257	4.077	1310
" " "	R. and G.*	66.37	1.239	3.91	1305
Ethyl benzene . . .	H., R. and L.	64.46	1.236	3.674	1375
" " "	R., S. and C.	64.31	1.228	4.35	1400
n Propyl benzene . . .	H., R. and L.	61.94	1.233	3.517	1453
o-Xylene . . .	R., S. and C.	65.52	1.250	3.94	1400
m-Xylene . . .	R., S. and C.	64.12	1.245	3.92	1390
" " *	W. and S.*	64.15	1.254	3.99	1386
n-Xylene . . .	H., R. and L.	62.23	1.22	3.93	1349
" " *	R. and G.*	64.40	1.252	3.74	1371
p-Xylene . . .	R., S. and C.	63.88	1.261	4.00	1383
" " "	H., R. and L.	63.10	1.254	3.85	1361
Chlorobenzene . . .	H., R. and L.	70.06	1.196	5.5	1396
" " "	<i>I.C.T.</i>	72.11	1.228	3.98	1383
Bromobenzene . . .	H., R. and L.	75.08	1.278	3.716	1478
" " "	<i>I.C.T.</i>	74.13	1.232	3.93	1460
Carbon tetrachloride .	<i>I.C.T.</i>	67.61	1.229	3.97	1221

TABLE I.—*Continued.*

Substance.	Authority.	γ_0 .	n .	p .	e_0 .
Cyclohexane . .	H., R. and L.	64.96	1.267	4.12	1263
Acetone . . .	H., R. and L.	66.00	1.212	3.925	972
Di-methyl ether .	M. and B.	61.48	1.247	4.089	803
Di-ethyl ether . .	R. and S.	56.72	1.252	4.15	1028
" " *	R. and S.*	59.02	1.241	4.13	1073
" " "	I.C.T.	57.37	1.232	3.92	1039
Ethyl bromide . .	H., R. and L.	67.97	1.188	3.67	1047
Ethyl iodide . .	H., R. and L.	72.61	1.224	4.17	1170
Propyl chloride .	H., R. and L.	66.01	1.269	4.266	1099

C. and M. = Coffin and Maass, *J.A.C.S.*, 1928, **50**, 1427.

M. and W. = Maass and Wright, *J.A.C.S.*, 1921, **43**, 1098.

H., R. and L. = Hennaut, Roland and Lek, *Bull. Soc. chim. belg.*, 1931, **40**, 177.

R., S. and C. = Richards, Speyer and Carver, *J.A.C.S.*, 1924, **46**, 1196.

H. and M. = Hunter and Maass, *J.A.C.S.*, 1920, **51**, 161.

R. and S. = Ramsay and Shields, *Trans. Roy. Soc.*, 1893.

W. and S. = Walden and Swinne, *Z. physik. Chem.*, 1912, **79**, 700.

R. and G. = Renard and Guye, *J. chim. physics*, 1915, **5**, 81.

R. and A. = Ramsay and Aston, *Z. physik. chem.*, 1894.

M. and B. = Maass and Boomer, *J.A.C.S.*, 1922, **44**, 1709.

I.C.T. = *International Critical Tables*.

Wa. and S. = Washburn and Shildneck, *J.A.C.S.*, 1933, **55**, 2354.

Sch. and K. = Schenck and Kintzinger, *Rec. trav. chim.*, 1923, **42**, 759.

When any figures bear an asterisk it indicates that the author's original figures have been corrected. See S. Sugden, *J.C.S.*, 1924, **122**, 1188.

It may be noticed in passing that the temperature variation of the free and total molecular surface energies, as usually defined, has been investigated along lines similar to those indicated² and it has been shown that the total molecular surface energy is not, as commonly assumed, independent of the temperature, but varies therewith according to a rather complicated law. For low values of the temperature, the variation is slight, the energy rising to a slight but definite maximum at a reduced temperature of 0.79, hereafter falling rapidly to zero at the critical point.

The quantities γ_0 and e_0 are functions of the critical constants; van der Waals has given reasons³ for putting

$$\gamma_0 = K\theta_c V_c^{-1}$$

where K is a universal constant and V_c is the critical *molecular* volume. Having determined values for γ_0 for a number of substances for which the critical data are available, we assumed that

$$\gamma_0 = K\theta_c^a V_c^b$$

and determined the constants K , a and b by the use of the method of least squares. We find that

$$\gamma_0 = 3.12 \cdot \theta_c \cdot V_c^{-0.85}$$

and the fit of this equation is tested later.

² Ferguson and Miller, *Proc. Physic. Soc.*, 1934, **46**, 140.

³ Van der Waals, *Z. physik. Chem.*, 1894, **13**, 716.

Similarly putting

$$e_0 = K_1 \theta_c^f \cdot V_c^g$$

we find, using the values of e_0 already deduced that

$$e_0 = 0.811 \theta_c V_c^{0.176}$$

But the parachor P is a simple function of e_0 and γ_0 and if we assume $p = 4$ we find that

$$e_0 = \gamma_0^{\frac{1}{2}} \cdot P^{\frac{1}{2}}$$

and therefore, on substituting the values of e_0 and γ_0 we have

$$P = A \cdot \theta_c^{\frac{1}{2}} V_c^{\frac{1}{2}}$$

The fundamental table in this paper is Table I. Here are tabulated values of γ_0 , n , p , and e_0 for a group of substances representing very

TABLE II.

Substance.	Temp. °C.	p .	$\frac{M\gamma^{\frac{1}{2}}}{\rho_L - \rho_V}$.	$\frac{M\gamma^{1.5}}{\rho_L - \rho_V}$.
Benzene (Sugden's figures)	20.0	3.91	205.9	209.9
	39.0	3.91	206.2	210.0
	54.8	3.91	206.2	210.1
	90.0	3.91	206.5	210.1
	150.0	3.91	206.8	209.9
Chlorobenzene (Sugden's figures)	12.0	3.95	243.6	246.3
	41.0	3.95	244.5	247.4
	81.0	3.95	244.7	247.3
	123.0	3.95	244.7	247.2
	180.0	3.95	244.3	246.3
Ether	20.0	4.12	211.6	207.3
	50.0	4.12	212.2	208.3
	80.0	4.12	211.1	207.3
	110.0	4.12	212.2	208.2
Methyl formate	50.0	3.98	138.0	138.7
	80.0	3.98	137.9	138.5
	110.0	3.98	138.1	138.6
	140.0	3.98	139.4	139.7
	170.0	3.98	139.2	139.5
Ethyl acetate	90.0	3.94	217.5	219.8
	120.0	3.94	218.8	218.6
	150.0	3.94	216.8	218.6
	180.0	3.94	217.2	218.6

varied types of organic liquid. To obtain data for these calculations we have searched the literature fairly thoroughly and critically, and our authorities are indicated in the second column. We have not thought it worth while to tabulate the values of $(n - 2n/3p)$ and $(n - 1 - \frac{2n}{3p})$ as these can be obtained at once from the table.

Given tables of critical data and of densities, it is possible from this table to calculate at any temperature trustworthy values of surface tension (γ), total surface energy (λ) and free and total molecular surface energies. It will be seen from the table that p deviates very sensibly

from 4 for a number of substances, and Table II. shows how the definition of the parachor as $(MC^{1/2})$ alters the values of P as compared with the value given by the fourth power law.

We have seen that it is possible to put empirically

$$e_0 = 0.811 \theta_c V_c^{0.176} \text{ and } \gamma_0 = 3.12 \theta_c V_c^{-0.55}$$

Table III. shows how closely these results are followed. In these columns e_0 (obsd.) and γ_0 (obsd.) refer to values calculated as described directly from the surface tension data; e_0 (calcd.) and γ_0 (calcd.) refer to values calculated by substituting values for the critical constants in the equations just given.

Table IV. similarly shows values of the parachors of various substances calculated from the equation

TABLE III.

Substance.	γ_0 (Observed).	γ_0 (Calculated).	e_0 (Observed).	e_0 (Calculated).
Methyl formate . . .	76.70	76.96	980	975
Methyl acetate . . .	67.26	68.57	1060	1066
Methyl propionate . . .	64.60	63.73	1169	1158
Methyl butyrate . . .	63.10	59.98	1270	1251
Ethyl formate . . .	67.50	68.54	1050	1070
Ethyl acetate . . .	63.92	62.34	1149	1146
Ethyl propionate . . .	59.34	58.69	1237	1235
Propyl formate . . .	62.69	64.25	1154	1177
Propyl acetate . . .	59.75	58.98	1240	1243
Ethane . . .	46.06	54.45	596	597
Propane . . .	57.45	54.89	763	757
Butane . . .	52.67	52.64	924	—
Isopentane . . .	51.29	52.92	1009	1022
Hexane . . .	53.41	52.77	1160	1159
Octane . . .	53.60	50.31	1373	1370
Acetylene . . .	62.12	62.34	621	575
Ethylene . . .	53.78	53.38	600	537
Benzene . . .	71.60	71.00	1210	1206
Toluene . . .	66.91	66.88	1310	1322
Chlorobenzene . . .	72.11	72.06	1396	1402
Bromobenzene . . .	74.13	74.21	1478	1499
Carbon tetrachloride . . .	67.61	67.55	1221	1210
Diethyl ether . . .	56.72	56.21	1028	1020

$$P = A\theta_c^{\frac{1}{2}} \cdot V_c^{\frac{1}{2}}$$

In this table are listed for comparison Sugden's values of the parachor as calculated from their elementary values. It will be seen that the agreement is reasonably good. (The value of A used in these computations is 0.324).

Finally, a preliminary and tentative attempt has been made to investigate the relation between chemical constitution and the values of e_0 and γ_0 . The usual procedure has been followed, a mean value for CH_2 being obtained, and values for carbon and hydrogen deduced by means of the paraffins. Values for other elements are then obtained, and the usual allowances may be made for the nature of the oxygen or other linking.

Such calculations suffer from paucity of data, and it is much to be hoped that anyone making a surface tension determination will obtain values over a wide range of temperature. It is only thus possible to obtain complete information concerning the surface energy of the liquid and its surface constants.

TABLE IV.

Substance.	$P(A\theta_c^{\frac{1}{2}}V_c^{\frac{1}{2}})$.	P (Sugden).
Methyl formate . . .	137.4	138.0
Methyl acetate . . .	177.3	177.0
Methyl propionate . . .	216.3	216.0
Methyl butyrate . . .	257.7	255.0
Ethyl formate . . .	178.4	177.0
Ethyl acetate . . .	218.4	216.0
Ethyl propionate . . .	259.5	255.0
Ethyl butyrate . . .	312.0	294.0
Propyl formate . . .	219.0	216.0
Propyl acetate . . .	260.4	255.0
Ethane . . .	104.3	112.2
Propane . . .	143.2	151.2
Hexane . . .	269.8	268.2
Octane . . .	357.3	346.2
Benzene . . .	201.8	207.1
Toluene . . .	245.3	246.1
Chlorobenzene . . .	243.8	244.3
Bromobenzene . . .	258.6	258.0
Carbon tetrachloride . . .	214.7	222.0
Acetylene . . .	84.7	90.4
Ethylene . . .	92.3	101.2
Diethyl ether . . .	209.7	210.2
Acetone . . .	169.9	160.2

From a comparison of the values of e_0 for different members of various homologous com-

pounds we find a mean value for CH_2 of 106 units. Combining this with the values for the paraffins we find in the usual way that the value for hydrogen is 262 units and for carbon *minus* 418 units. For oxygen in the ether group the value is 74.5 units.

With these figures it is possible to make a rough comparison of the calculated and observed values of ϵ_0 . These are shown in Table V.

These figures are, however, merely a preliminary contribution; the present paper is chiefly concerned with the calculation and listing of the more important surface tension constants. We hope, in a later paper, to discuss the effects of composition and constitution in some detail.

TABLE V.

Substance.	ϵ_0 (Observed).	ϵ_0 (Calculated).
Dimethyl ether .	803	810.5
Methyl ethyl ether .	917	916.5
Diethyl ether .	1028	1022.5
Ethyl propyl ether .	1130	1128.5
Ethane . . .	596	736
Propane . . .	760	842
Butane . . .	924	948
Pentane . . .	1047	1054
Hexane . . .	1160	1160
Heptane . . .	1269	1266
Octane . . .	1373	1372
Decane . . .	1596	1584

Note by A. F.

The work has been made possible by the assistance of a grant from the Department of Scientific and Industrial Research, and I desire to offer my thanks to the Advisory Council of the Department for their assistance, and to Prof. H. R. Robinson who has given every facility for the prosecution of the investigation.

REVIEWS OF BOOKS.

Die Allotropie der chemischen Elemente und die Ergebnisse der Röntgenographie. By M. C. NEUBURGER. Stuttgart: Ferdinand Enke, 1936. Pp. 106, with 32 illustrations. Price R.M. 9.30.

The author has performed a valuable service in bringing together the results of scattered observations dealing with the general subject of allotropy. Most of the book is composed of a systematic review of the elements, reinforced with brief discussions of the influence of impurities, atomic properties, and the mechanism of transformations. Within limits, this is all that could be expected, and the monograph does not set out apparently to be the last word on this aspect of energetics. Nevertheless, one or two comments may be offered.

To take details first (since they concern the systematic part of the book), one would hesitate to subscribe to the view that bismuth shows only one form. It is hard to say exactly, but magnetic work of the greatest delicacy seems to imply that this substance passes through a number of allotropic changes packed very closely together (on a temperature scale) just beneath the melting-point. Again, it may be true that iodine is not allotropic: it is very difficult to credit it; not because definite proof of two forms can be advanced, but for theoretical reasons.

Allotropy is a subtle and fascinating study, and those who indulge in it need a special flair, which enables them intuitively to track down its existence; convictions exist that something is allotropic, and years may go by in establishing it. Furthermore, the phenomenon may be substructural, and X-ray analysis may therefore not be conclusive. These thoughts, however, do not detract from the value of Dr. Neuburger's book; we shall turn to it for help very often.

F. I. G. R.

Theory of Machines. By LOUIS TOFT, M.Sc., and A. J. T. KERSEY (third edition). London: Sir Isaac Pitman & Sons, Ltd. 12s. 6d.

This is a new edition of the well-known text-book for engineering students. The opportunity has been taken to add some notes on boundary lubrication to Chapter VII. dealing with Friction and the Theory of Lubrication, and also to explain the tabulation method of treating problems on epicyclic trains—a method which many students have found helpful. The chapter on Oscillations and the Whirling of Shafts has been extended to deal with modern developments in high speed internal combustion engines.

Chromium Plating: with Special Reference to Its Use in the Automobile Industry. By O. BAUER, H. ARNDT, and W. KRAUSE. Translated from the German by E. W. PARKER. London: Edward Arnold & Co., 1935. Pp. vi + 266. Price 25s.

In view of the great importance of chromium plating to the automobile industry, the authors of this book, O. Bauer, H. Arndt and W. Krause, working under the auspices of the German State Bureau for Testing of Materials, carried out an extensive investigation on the properties of actual specimens of plated automobile parts. The principal aim of this work was to obtain data of a reliable and unbiased character which could be placed at the disposal of the industries concerned, with the object of raising the general standard of commercial chromium plating. The results were published as an official German report, and a translation of this forms the basis of the present book. The text has been modified by the introduction of additional material which provides a fuller survey of English, American and Continental practice than was given in the original report, and the bibliography has been greatly extended in this connection and also brought up to date. In addition a short introductory chapter relating the properties of nickel and chromium deposits to electroplating practice has been written by A. W. Hotherhall.

The title of the book is somewhat misleading: not more than a page or two is actually devoted to the practice of chromium plating, most of the subject-matter dealing with the testing of chromium-plated articles. The chief headings under which the tests are described are: surface quality; adhesion; hardness and wear-resistance; resistance to high temperatures and reversal of temperature; porosity; and corrosion resistance. It is certain that the investigations have been carried out with marked thoroughness, and the large number of tables, diagrams and photographs aid materially in making the results clear to the reader. A valuable and

concise summary of the conclusions to be drawn from the work are given in the final chapter. The bibliography, which contains nearly 600 references, is mainly concerned with papers and books published between 1920 and June 1935; patent literature as such is not included, but references are given to publications in which patent claims are considered.

The translator and publishers have done their work well: the price of the book is high for its size, but this is undoubtedly due to the expense involved in the high-class reproduction of some 190 half-tone plates. The book can be recommended to all organisations concerned with chromium plating or with the use of chromium-plated materials.

S. G.

Electron Emission and Adsorption Phenomena. By J. H. DE BOER; Translated from the manuscript by MRS. H. E. TEVES-ACLY. Cambridge University Press, 1935. Pp. xi + 398. 21s. net.

The object of this book is to co-ordinate for the first time what may be called the physics and the chemistry of surfaces. It gives a connected story of electron emission from metals and the adsorption of atoms on their surfaces. After two excellent introductory chapters on thermionic emission and the nature of adsorption forces a detailed account is given of the influence of adsorbed layers on the emissive properties of metals, particularly of caesium and similar atoms on tungsten. After a statement of the facts observed by Langmuir, Becker and other workers, the author shows that it is possible to construct a satisfactory picture of the nature of adsorbed layers on metallic surfaces from the phenomena of thermionic emission. He then examines the extent to which this picture is in accord with the results obtained in photoelectric emission and shows that the main facts can be readily explained. The selective photo effect is shown to be the result of the absorption of light by adsorbed atoms and hence it is useful as an indicator of the presence of neutral atoms as well as ions on a surface.

In the second part of the book the properties of alkali metal atoms adsorbed *within* dielectrics are discussed and their photoelectric properties are compared with those adsorbed on surfaces. The absorption of light of suitable wave-length can produce photoionisation but, since the electrons thus ejected must have energies which lie between definite limits determined by the lattice structure of the dielectric, the absorption spectrum has certain characteristic differences from that of the same atoms adsorbed on the exterior surface. The movement of the ejected electrons within the solid produces that interesting set of phenomena described as photoelectric conductivity, an account of which the book provides.

This is a particularly interesting book written from a novel point of view. The style is simple and easy, being non-mathematical and descriptive, and the English, though a translation, is surprisingly good. It is marred only by one or two unusual descriptive terms, such as "ionisation tension" instead of the usual English "ionisation potential" (p. 143). There is a free use of potential curves to represent visually energy relations of all kinds, which greatly adds to the interest and enjoyment of the reader.

J. E. L.-J.

The Principles of Quantum Mechanics. By P. A. M. DIRAC. Second Edition. Oxford: Clarendon Press, 1935. Pp. xi + 300. Price 17s. 6d.

This is a revised edition of a book which is generally accepted as the most logical and authoritative exposition of the laws of quantum mechanics yet produced. The presentation has been changed so as to reduce the abstract character of the first edition, and is likely to appeal to a wider circle of readers.

The main alteration centres round the use of the word "state." A satisfactory system of mechanics must provide a method of dealing with the relations and laws of nature governing the state of affairs in an atomic system at one instant of time and must also show the connection between the state of affairs at one instant of time with those at other instants of time. The new use of the word "state" is to make it refer to the condition of the dynamical system at one instant of time, and so the "state" of a dynamical system may be regarded as continually changing under the influence of the equations of motion. This new definition is non-relativistic, as it refers to conditions in a three-dimensional section of space-time belonging to one time-instant. The author expresses the view that this concept of "state" facilitates a clear exposition of the subject and induces the belief that probably the fundamental ideas of the present quantum mechanics need revision at just this point.

Another change from the first edition is the addition of a chapter on the quantum theory of the electromagnetic field, but the present formulation of this theory is very complicated and, as the author points out, it has not yet produced any results which cannot be obtained by more elementary methods. A satisfactory theory of the radiation field and its interaction with matter has not yet been produced.

This edition, like the first, is a model of clear and logical exposition. It is expressed in simple language even when the ideas involved are complex. It is a scholarly book and can be thoroughly recommended to all who seek a clear formulation of the laws of quantum mechanics as they stand at present.

J. E. L.-J.

Thorpe's Dictionary of Applied Chemistry. Supplement. Vol. III., Glossary and Index. By J. F. THORPE and M. A. WHITELEY. (London: Longmans, Green & Co. Pp. 166 and vii. 21s. net.)

This concludes the labour of bringing the last edition of Thorpe up-to-date. Those who have used Vols. I.-VII. have well realised the utility of the Index in Vol. VII. An index to the two supplementary volumes was therefore keenly awaited. Needless to say, it has been well done. This volume also includes a glossary of terms, which will often be helpful.



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Died 25th August, 1936.

WILLIAM RINTOUL

President of the Faraday Society, 1934 to 1936

MR. WILLIAM RINTOUL died at his home in Ardrossan on the 25th of August at the age of sixty-six. He was educated at Anderson's College, Glasgow, and received further chemical training in the laboratories of Mr. R. R. Tatlock, one of the few schools of analytical chemistry. He was for a short time an assistant and then a lecturer in chemistry to Tatlock's students. In 1891 he came to London as chemist to a paint manufacturer, but in 1894 started out on his life-work. First at Waltham Abbey with his friend Robert (now Sir Robert) Robertson, under Sir Frederic Nathan, and, after 1909, at the Ardeer factory of Nobel's Explosives Co., whither he accompanied Sir Frederic, he was concerned in the safety and efficiency of manufacture of explosives. As research manager at Ardeer he reorganised the laboratories and started new ones, as, for example, for biochemical and physical work; his policy, specially in regard to the organisation of the work of his laboratories and the documentation of these results and of relevant work published in the literature, has been the model for many other research organisations. When Nobel's joined Imperial Chemical Industries, Rintoul came to London as joint research manager of the larger organisation, and here his organising abilities found even fuller scope; his correlation of industrial and academic research will be specially remembered.

He gave generously of his time to the work of councils and committees, serving on the Councils of the Chemical Society, and of the Institute of Chemistry and on the Federal Council, the Safety in Mines

Research Board, the Chemistry Research Board (D.S.I.R.), the Research Committee of the L.M.S. Railway and the British Standards Institution. As a representative of his firm he was well-known abroad, and he often attended meetings of scientific societies in this country and on the Continent. For his work in the Great War he was made an O.B.E.

He married first Lottie Edwards, by whom he had two sons and a daughter, and, two years ago, Jess Isabel Robertson, the sister of his former colleague.

Rintoul served on the Council of the Faraday Society continuously from 1930, and in October, 1934, he became President. He took a living interest in the work of this Society and especially in the formation of the Colloid Committee, of which he was an original member. His enthusiasm for the Colloid meetings, a subject to which he was perhaps drawn from his acquaintance with gelatinised nitrocellulose, culminated in the very successful meeting on the Phenomena of Polymerisation and Condensation, which was held at his suggestion and under his presidency.

He will long be remembered by those who were privileged to attend the meetings under his presidency at the Imperial College in April, 1935, and in Cambridge in September, 1935, where his tact in conducting the business and the charm of his personality, evinced both during the meetings and informally in his room, as host, made those meetings an outstanding success. Shortly after the Cambridge meeting news was received of his serious illness, but, though he was unable to preside at the spring meeting of 1936, he looked forward with special joy to welcoming the Society in the autumn to his home country; his absence from the Edinburgh meeting gave added poignancy to the Society's loss.

It is given to few men to have made so many real friends.

SOME NEW ULTRAVIOLET BANDS OF SO, IN EMISSION.

BY G. KORNFELD.

Received 2nd July, 1936.

In a previous investigation¹ an electrodeless discharge passing through SO₂ had been used to obtain the emission bands of SO. On casual observation it was then found that the spectrum obtained on the photographic plate extended to nearly 2100 Å. if the exposure was taken through the wall of the tube, whereas the spectrum taken as usual through the plane end extended only to about 2400 Å. This observation was easily explained since the absorption of SO₂ in this region has been found to increase again towards shorter wave-lengths² and since the discharge occurred in a ring against the wall, whereas its distance from the plane end was not much less than 1 cm.

From more than one point of view it seemed interesting to investigate this new part of the emission spectrum. First of all it was important to make sure that the emission band system of SO did not extend farther to the ultra-violet than with the last band previously observed.³ Since predissociation has been assumed in this region⁴ on the basis of the experimental result, and since the energy of dissociation of SO has been calculated on this assumption, it seemed worth while to find out whether this result was established beyond doubt, and whether, even if the bands should be found to continue to shorter wave-lengths, there would be a break at least in the critical region. On the other hand, if the bands should be found not to belong to this system of SO or perhaps not to SO at all, it seemed important to ascertain to which of the partaking ions or molecules they could be ascribed.

Experimental Procedure.

The sulphur dioxide used in this investigation was first carefully prepared by a method already mentioned⁵ but, however carefully employed, the CO bands were always present in the ultra-violet region. A much simpler method proved, however, to be successful: the quartz discharge tube was connected at one end to a flask containing liquid SO₂, and at the other end—through a large tube filled with KOH—to an ordinary Hyvac pump. By regulating the taps on both sides a suitable pressure for the discharge could easily be maintained during the exposure. With this method no CO bands were visible on the plate.

The electrodeless discharge was maintained by an oscillator with a powerful valve (used at 125 milli amps.) connected to a generator yielding

¹ G. Kornfeld and M. McCaig, *Nature*, 1935, 135, 185.

² G. Kornfeld and E. Weegmann, *Z. Elektroch.*, 1930, 96, 93.

³ V. Henri and F. Wolff, *J. Physique et Radium*, 1929, VI, 10, 81.

⁴ E. V. Martin, *Physic. Rev.*, 1932, 41, 167.

⁵ G. Kornfeld and M. McCaig, *Trans. Farad. Soc.*, 1934, 30, 991.

up to 3000 volts. The electrodes, separated by about 7 mm. from one another, were adjusted round the tube ($d = 25$ mm.).

The colour of the discharge depended on the pressure; at low pressures it was a vivid violet, changing towards blue with increasing pressure, until the discharge showed a strong blue colour. At still higher pressures the discharge could not be maintained. The numerous bands in the region below 2400 Å. could not be found in the spectrograms of the violet discharge, but only of the blue discharge. The investigation of the new bands was therefore carried out with the discharge of blue colour; this blue light was continuous in the visible region and there was also a very strong continuous spectrum in the ultra-violet region, diminishing gradually to about 2300 Å. The long exposures needed for the bands below 2400 Å. made the continuous spectrum rather strong in the region of longer wavelengths. During the exposure the pressure had to be carefully regulated by adding a small amount of SO_2 , whenever the colour began slightly to change, owing to diminishing pressure of SO_2 , arising from its decomposition, as was clearly demonstrated by the large amount of sulphur deposited on the walls of the tube (outside the region of the discharge).

The spectrograms were taken with a medium size quartz spectrograph (Hilger E2) with a dispersion of 8 Å. per mm. at 2400 Å.

The Spectrum of the Discharge.

Down to about 2440 Å. the continuous spectrum was very strong on the photographic plate and accordingly there the bands were only faintly visible; in the region of shorter wave-lengths, however, which was the object of this investigation, the bands could be seen clearly enough to be measured.

Fig. 1 is an enlarged negative print (the emission bands and lines are seen to be dark against the white background) of this band spectrum together with the line spectrum of an iron arc. The numerous bands, varying somewhat in intensity, are slightly degraded to the red; in most of them there is no structure, only in a few can some faint traces of structure be detected.

In the region between 2180 and 2150 Å. some bands are just visible, though not sufficiently clearly to be registered. But most of the bands could be registered and were measured by comparing them with the lines of the iron arc and the copper arc, the latter being used for the farther end of the ultra-violet region.

The Analysis of the Spectrum.

In Table I. all the band heads of the region below 2443 Å. are given in Ångström units. Fourteen of them, indicated by brackets, coincide within 1 Å. with known absorption bands* of SO_2 ; considering, however, that

TABLE I.

2442.5 ⁺	2377.6	(2326.0)	2280.5	2235.7 ⁺	(2188.1)
2433.0	2372.1	2319.6	2279.7 ⁺	2232.4 ⁺	(2185.2)
2429.0 ⁺	2368.5	2315.6	2274.6 [*]	2228.3	2181.5 [*]
2421.5 ⁺	2360.3 [*]	2311.7 ⁺	2271.6	(2222.0) [*]	(2168.5) [*]
2414.1	2357.0 ⁺	(2306.9)	(2267.7)	2216.2 [*]	2150.5 [*]
2404.0	2350.7 [*]	2301.8 ⁺	2266.5	2214.8	(2140.8)
2399.0	(2348.5)	2299.6	(2260.2)	2211.5 [*]	(2135.4)
2395.7 ⁺	2339.4 ⁺	2294.0	2256.0	(2205.3) [*]	2122.5 ⁺
2388.5 ⁺	2333.0 ⁺	(2288.6) [*]	(2248.3) [*]	2195.7 ⁺	
2382.5	2330.1 [*]	(2287.5) [*]	(2241.5) [*]	2191.3 ⁺	

* T. Ch. Chow, *Physic. Rev.*, 1933, 44, 683.

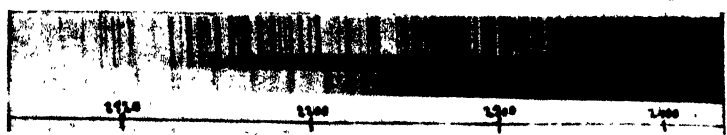


FIG. 1.

To face page 1488.

the discharge occurred close to the wall, practically no absorption should be expected to be visible on the plate, especially in the region about 2300 Å., where the intensity of absorption is comparatively small.¹ On the other hand, an accidental coincidence of so many bands seems rather improbable, unless they belong to the same system, which means that in this case they should belong to SO_2 in emission. In the positive column of a discharge passing through SO_2 , Chow² has found numerous new emission bands between 2600 and 2040 Å. of which twenty-eight coincide with bands given in Table I. (some coinciding also with the absorption bands) and are there italicised. Sixteen of these twenty-eight (asterisked) have been identified by Chow as belonging to the emission of SO_2 , and some of them can be found also amongst W. Lotmar's³ fluorescence bands; with which sixteen further bands of Table I. (marked +) have been found to coincide, so that only ten bands are left which were not known. An attempt to arrange these ten (as well as the others) in accordance with the band system of SO proved unsuccessful, and thus the possibility of SO emission bands existing beyond the assumed limit of predissociation has been negatived. It seemed reasonable to try whether these bands could not be ascribed, along with the others, to the emission band system of SO_2 .

The frequencies of the normal electronic state of SO_2 , ν_1 , ν_2 , and ν_3 , have lately been determined by various authors. Lotmar, investigating the fluorescence spectrum of SO_2 , found the values 1150, 520 and 1370 cm^{-1} (in his numbering ν_1 , ν_2 , and ν_3), well agreeing with the Raman frequencies.⁴ These values, especially the first two, were confirmed by Chow and by H. D. Smyth⁵ and quite recently by J. H. Clements¹⁰ in his investigation of the absorption spectrum between 3300 and 2600 Å. This spectrum belongs to another upper level than the absorption spectrum in the farther ultra-violet region, but both systems share the same initial level; the absorption spectrum in the farther ultra-violet region¹¹ has been found to share both electronic levels with the fluorescence bands of Lotmar and with the emission bands of Chow. For the upper level Lotmar found the progression 390 cm^{-1} or a multiple, Chow found 375 cm^{-1} or a multiple for the absorption bands; in his scheme for the emission bands he assumed three different progressions, one of which he took to be 750-770 cm^{-1} , whereas the others were still uncertain.

The wave-numbers of the bands of Table I. proceed along the three progressions, 380, 500 and 1140 cm^{-1} ; from the above-mentioned investigations the first is likely to belong to the upper level, while the other two coincide with two frequencies found for the ground level; there is no evidence for a progression along the third fundamental frequency, 1370 cm^{-1} . The bands have accordingly been arranged in a scheme represented by Tables II., III. and IV. Assuming that $\nu_1'' = 1140 \text{ cm}^{-1}$, $\nu_2'' = 500 \text{ cm}^{-1}$ and, tentatively, that 380 cm^{-1} could be ascribed to ν_3' , each table represents two progressions along ν_1' and ν_2'' respectively, the mean values for ν_3' being: 377, 403, 381, 381, 386, 384 and for ν_2'' : 500, 499, 506; the mean differences from one table to another are 1143 and 1140 cm^{-1} , in good agreement with a progression along ν_1'' . The bands coinciding with absorption bands are again marked by brackets; bands used in more than one table are italicised; in a few cases the wave-numbers have been corrected to fit in better with the scheme, the difference between both values being about 20 cm^{-1} and never amounting to more than 30 cm^{-1} ; where this has been done the original values are indicated below the new ones.

The arrangement seems to be satisfactory although, considering that $3\nu_1' \sim \nu_1''$, it cannot be taken as final: there are other possibilities; if

¹ W. Lotmar, *Z. Physik*, 1933, 83, 765.

² A. Dadiou and K. W. F. Kohlrausch, *Physik. Z.*, 1932, 33, 165.

³ H. D. Smyth, *Physic. Rev.*, 1933, 44, 690.

¹⁰ J. H. Clements, *Physic. Rev.*, 1935, 47, 224.

¹¹ K. Wieland, *Nature*, 1932, 130, 847.

TABLE II.

$v' = b.y.o$ $\downarrow \quad \rightarrow$ $v'' = (a+1).x.o$	$y = n.$	$y = n + 1.$	$y = n + 2.$	$y = n + 3.$	$y = n + 4.$	$y = n + 5.$	$y = n + 6.$	$y = n + 7.$
$x = m$	(43681)	(44084)	44464	44843 63	45204	45621	(46070) 100	46486
$x = m + 1$	43172	43579	43950	(44342) 12	44717	45108	45529	
$x = m + 2$	42733	43098	43472	43852	(44230)	(44599)	(44990)	
$x = m + 3$	42144	(42567)	(42979)					

TABLE III.

$v' = b.y.o$ $\downarrow \quad \rightarrow$ $v'' = (a+2).x.o$	$y = n.$	$y = n + 1.$	$y = n + 2.$	$y = n + 3.$	$y = n + 4.$	$y = n + 5.$	$y = n + 6.$
$x = m$	42527	42903	(43335)	(43702)	44107		
$x = m + 1$	42046	42414	42850	43225 45			
$x = m + 2$		41930 60	42354	42733	43098	43451 31	43836
$x = m + 3$			41855	42228 08			

TABLE IV.

$v' = b.y.o$ $\downarrow \quad \rightarrow$ $v'' = (a+3).x.o$	$y = n.$	$y = n + 1.$	$y = n + 2.$	$y = n + 3.$
$x = m$	41411	41759 29		
$x = m + 1$	40929	41284	41691 71	
$x = m + 2$	Region of strong continuous emission, Bands not clearly visible.		41187 57	41585
$x = m + 3$				41086

more coincidences be assumed to occur, Tables III. and IV. would contain many additional bands. Even accepting this, however, no conclusive evidence can be given for the absolute numbering of the progressions; m and n , a and b are not defined, even if it is assumed that ν_1 in both levels is not excited. An indication, however, might be found in Table V. which

TABLE V.

$\begin{array}{c} \nearrow v' = b, y, 0 \\ \searrow v'' = a, x, 0 \end{array}$	$y=n$	$y=n+1$	$y=n+2$	$y=n+3$	$y=n+4$	$y=n+5$	$y=n+6$	$y=n+7$	$y=n+8$
$x = m$						(46815)			
$x = m + 1$			45137						
$x = m + 2$						45826		(46697)	47093
$x = m + 3$						(45331)	(45748)		
$x = m + 4$				44008		44783		(45687)	

contains the rest of the bands—with a mean difference of 1200 cm^{-1} from those in Table II. Now Clements found 1200 cm^{-1} to be the difference between the first and the second vibrational level belonging to ν_1'' , so that a should be equal to unity. Supposing that $m = 0$ and $n = 0$, the wave-number for the transition between the upper level with $v' = b, 0, 0$ and the ground level with $v'' = 0, 0, 0$ should be $46,050 \text{ cm}^{-1}$. For ν_1 Chow found $45,757 \text{ cm}^{-1}$: the difference of 300 cm^{-1} should then be accounted for by ν_1' .

These latter suggestions are, however, only tentatively made, since the level indicated by Table V. contains only a few scattered bands; moreover, the difference of 1200 cm^{-1} might instead belong to the upper state, and then a could not be determined at all.

Apart from these conclusions concerning the numbering of the vibrational levels the scheme works satisfactorily since it contains all the bands. The combined levels of ν_1'' and ν_2'' seem to be characteristic of this special scheme; in Chow's paper the levels α_1 and α_2 are given, corresponding to $1\nu_1'' + 1\nu_2''$ and $1\nu_1'' + 2\nu_2''$ respectively, but no levels are mentioned which would correspond to the higher numbers combined in this investigation. Such levels, however, could be derived from the progressions of Lotmar's fluorescence bands; the small amount of coupling, too, between ν_1'' and ν_2'' (ν_1'' and ν_2'' in Lotmar's numbering) is in good agreement with Lotmar's experience. It seems, however, that the exclusive preference of these levels must be ascribed to the special conditions of the high frequency discharge. The absence of any transitions including a change in ν_3 seems to be another characteristic feature of this discharge.

Summary.

An electrodeless discharge of a strong blue colour passed through SO_2 along the walls of a quartz tube through which a spectrogram was taken. Between 2443 and 2120 \AA . the heads of fifty-nine bands were measured, of which forty-nine coincided with bands known to belong to SO_2 . Neither these nor the remaining ten could be added to the known system of SO bands, so that there is no evidence of any emission bands beyond its established limit of predissociation. All the bands are consistent with the

known band system of SO_2 in emission, and a special scheme has been suggested where the vibrational levels of the ground state are combined of higher numbers of ν_1 and ν_2 .

The experimental part of this work was done at the Astrophysics Department of the Imperial College in London. The author desires to thank Professor G. P. Thomson and Professor H. Dingle for their hospitality. She is specially indebted to Dr. R. Pearse for his helpful and constructive criticism then and afterwards. Many thanks are further due to Hofrat Professor Mache of the *Physikalisches Institut der Technischen Hochschule* in Vienna for kindly allowing the use of his comparator. Finally, the author wishes to thank the American Association of University Women for the International Fellowship of this academic year which enabled her to carry out this investigation.

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NOTE ON THE MECHANISM OF CATALYTIC INTERCHANGE OF HYDROGEN WITH WATER AND ALCOHOL.

BY JURO HORIUTI AND GO OKAMOTO.

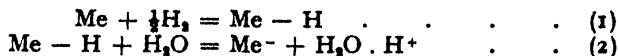
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The authors have observed previously¹ that a nickel sheet operates as a reversible hydrogen electrode at 50°C. The main points of their observation with this hydrogen electrode are as follows:

(1) The rate of interchange of hydrogen with the solution at varying electrode potential over a range of a few tenths of a volt, remains constant within a factor 1 to 2.

(2) When the hydrogen electrode in the reversible state is positively polarised, the initial current decreases gradually, tending to a definite value. When, further, the polarisation of the electrode in the steady state is decreased, the small initial current increases gradually, tending again to a definite value. This final steady current, can be reproduced by arranging the partial pressure of hydrogen and the polarisation.

Assuming that these processes² take place in two steps,



it was concluded that the rate determining step is the first one, i.e. atomisation of hydrogen molecule on the metal. The second step is the ionisation of atoms. The argument which leads to this conclusion will be briefly reproduced here.

Electrode potential changes only the rate of ionisation. Assuming that the bond $\text{Me} - \text{H}$ is homopolar, the first step is not appreciably influenced by the electrode potential. If it were polar (e.g. $\text{Me}^- - \text{H}^+$) either atomisation or ionisation is the rate-determining step. If atomisation, the second experimental fact can always be explained while the small variation

¹ Horiuti and Okamoto, *Sc. Pap. I.P.C.R.*, 1936, **28**, 231

² Another mechanism was suggested for the electrode process on poor recombination catalysts, such as Hg and Sn.

of interchange reaction rate might partly be attributed to the effect of the influence of the electrostatic field. If ionisation, the concentration of $\text{Me}^- - \text{H}^+$ should increase initially on raising the electrode potential, since the energy of $\text{Me}^- - \text{H}^+$ is lowered, and the current should increase initially; this is contrary to experiment. It is highly improbable that the second step is the rate determining one and the opposite polarity $\text{Me}^+ - \text{H}^-$ since the electron affinities of nickel and hydrogen are 4.9 and 0.7 volts respectively. It follows that the observed result (1) can only be explained by adopting atomisation as the rate determining step.

Further if $\text{Me} - \text{H}$ were in incipient equilibrium with $\text{Me} + \frac{1}{2}\text{H}_2$, the concentration of $\text{Me} - \text{H}$ should be constant, independent of polarisation. The steady current must be obtained immediately after polarisation. Alternatively, the concentration of $\text{Me} - \text{H}$ should increase or decrease with the rate of ionisation until the new preliminary equilibrium at the given polarisation is set up. It follows that the current should initially decrease or increase according as the positive polarisation is raised or lowered. The two experimental facts can be thus only accounted for by assuming the atomisation as the rate determining step.

Following the program announced in the previous paper¹ the writers have calculated the theoretically absolute values of anodic and cathodic currents, interchange reaction rates and isotopic separation factor; they are in fair agreement with the experimental results, the concluded rate determining step and the homopolar bond $\text{Ni} - \text{H}$ being assumed as the basis of the calculation.³ Moreover Tafel's empirical relation as to the overvoltage could be derived.

The question as to the rate determining step for the electrode process seems to have been thus settled, so far at least as nickel metal is concerned.

The authors do not feel fully justified, however, in extending the conclusion to the case of platinum. In the work of Hirota and one of us which will soon be published, it is shown that the interchange rate of hydrogen with water in the presence of platinum is 10^6 times greater than in the case of nickel for the same apparent area of catalyst. This difference corresponds to the activation energy of 7 K cal., if the temperature independent factor remains approximately the same in both cases. In another work of Hirota, the activation energy of the interchange reaction on nickel was determined as 13 K cal. The activation energy with platinum should accordingly be 6 K cal., instead of 10.2 K cal. as observed by Polanyi in conjunction with one of us.⁴ This is, of course, a very crude estimate, but some doubt persists whether the rate determining step is really the atomisation in the case of platinum too. Further complication is to be expected, if the rates of both steps are comparable for, according to the theory of Volmer⁵ and Frumkin⁶ as extended by Polanyi in conjunction with one of us,⁷ the height of the potential barrier for ionisation varies with the electrode potential and, consequently, with the nature and acidity of the solution. It is, therefore, conceivable in this case that either of the two steps alternately governs the rate.

More recently Eley and Polanyi have conducted extensive experiments on the *para-ortho* conversion of hydrogen together with that on the interchange rate of hydrogen with water and alcohol in the presence

¹ G. Okamoto, J. Horiuti and K. Hirota, *Sc. Pap. I.P.C.R.*, Tokio, 1936, 19.

⁴ J. Horiuti and M. Polanyi, *Trans. Manchester Lit. Phil. Soc.*, 1933-34, 78, 47.

⁵ Erdey-Gruz and Volmer, *Z. physik. Chem.*, A, 1930, 150, 209.

⁶ Frumkin, *ibid.*, A, 1932, 162, 53.

⁷ Horiuti and Polanyi, *Acta Physicochim.*, U.S.S.R., 1935, 2, 505.

of platinum black.⁸ They found (1) the first order rate of the spin conversion k_p is 2 to 3 times greater than that for the isotopic replacement k_d in most of their cases, although approximately equal in some cases. (2) Both the rates are faster in acid solution than in alkaline. The difference is most pronounced in the case of alcohol: addition of alkali reduces the rate by a factor 4.

Eley and Polanyi conclude provisionally from these results that the rate determining step is the atomisation of hydrogen molecules in accordance with our previous conclusion for nickel.¹ In order to account for the second result Eley and Polanyi assume that the rate of atomisation is influenced by the electrode potential, the product of splitting being strongly polar.

We will now consider here some possible alternatives which also fit their experimental results.

Admitting the suggested polarity of the product of atomisation, the observed parallelism between k_p and k_d would equally follow, whether it is atomisation or the ionisation which governs the rate, since the rate of atomisation would then vary, along with the ionisation, with variation in the electrode potential. Atomisation as the rate determining step is no more conclusive. If the ionisation is slower, however, k_p/k_d must be greater than in the opposite case. By poisoning the catalyst, *i.e.* by reducing the rate of the atomisation k_p/k_d must be lowered, as is seen from their results.

Assuming on the other hand the homopolar bond $Pt-H$, it is possible that it is the atomisation which governs the rate. It remains now to explain the observed effect of acidity. It is possible that this rather small effect is due to poisoning; it is well known that the poisoned platinum catalyst may be reactivated by oxygen. Eley and Polanyi attribute the sudden increase of catalytic activity observed in the course of their experiment to the admission of air. In the operation of changing the solution from acidic to alkaline the catalyst must be brought in contact with air-containing liquid. Deactivation by the poison contained in alkali and subsequent reactivation by air might possibly be the cause of the observed "reversibility." To clear the matter up, it is desirable to perform experiments with solutions previously depoisoned by keeping them for some time in contact with platinum catalyst, as has been done by Volmer and Wick.⁹

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⁸ Eley and Polanyi, *Catalytic Interchange of Hydrogen with Water and Alcohol*. This vol. p. 1388.

⁹ Volmer and Wick, *Z. physik. Chem., A*, 1935, **172**, 429.

THE CATALYTIC ACTION OF HYDROGEN ON THE CARBON MONOXIDE FLAME.

BY HENRY JAMES WALLS.

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The mechanism of the reactions occurring in the carbon monoxide flame is still far from clear. But in most of the various schemes of reaction which have been put forward, the processes, once the flame has been started, are assumed to be mainly homogeneous. The facts presented below, however, suggest that the nature of the walls has a considerable influence on the course of the reaction. Garner and his co-workers have established ^{1, 2, 3} that when the infra-red radiation emitted from the explosion of a carbon monoxide-oxygen mixture containing hydrogen is plotted against the initial pressure of the gas, a "step" or discontinuity in the curve occurs, indicating a sudden change at a given pressure in the amount of radiation emitted. The pressure at which this step occurs is connected with the partial pressure of hydrogen in the mixture by the equation ⁴

$$(p_s \times p_{H_2} + 0.018p_s)/3.28 = 1 \quad . \quad . \quad (I)$$

where p_s is the pressure at the step, and p_H is the pressure of hydrogen for which the step occurs at p_s .

It is noteworthy that p_s is hardly affected by the nature of the material composing the vessel in which the combustion takes place, and that it is increased by the addition of carbon dioxide, chlorine, or bromine to the explosive mixture,^{3, 4} while it is unaffected by a 33 per cent. increase in the concentrations of either carbon monoxide or oxygen.²

Garner and Pollard⁴ have discussed two possible explanations for the existence of this step, *viz.*,

(a) that the step represents a lower limit for the propagation of a hydrogen flame in a carbon monoxide-oxygen mixture, or

(b) that the step is the pressure at which two mechanisms of combustion (presumably involving, and not involving hydrogen, respectively; the latter case may be either an oxygen atom or a thermal chain; see *e.g.*, Alyea⁶) produce flames travelling at equal speeds. The authors decide that (b) is the most probable explanation.

The newer theories of explosion, however, largely developed by Semenov and his school, provide us with a method for settling this question definitely. For an explosive gaseous mixture the lower limit of ignition is connected with the temperature by the equation ⁶

$$\log p = \frac{A}{T} + B \quad . \quad . \quad . \quad . \quad (2)$$

¹ Garner and Hall, *J.C.S.*, 1930, 2037.

³ Garner, Hall and Harvey, *J.C.S.*, 1931, 641.

³ Bawn and Garner, *J.C.S.*, 1932, 129.

⁴ Garner and Pollard, *J.C.S.*, 1935, 144.

^b Alyea, *J. Amer. C.S.*, 1931, 53, 1324.

* Semenoff, *Chemical Kinetics and Chain Reactions*, p. 83.

where A and B are constants. It is obvious that if hypothesis (a) is correct, *i.e.*, if the step represents a definite lower ignition limit, the step must move to lower pressures as the temperature increases; conversely, if increase of temperature raises p_s , (a) cannot be correct, and (b) is then the most probable explanation. This question was tested experimentally, and it was found that p_s rises with temperature.

Experimental.

The apparatus was similar to that used by Garner and Roffey for measuring the radiation from gaseous explosions.⁷ The purified, mixed and dried gases were exploded in a quartz bomb, about 30 cm. long and 2 cm. diameter, by the fusion of a small piece of very fine platinum wire. The radiation was received on a quick-acting linear thermopile, which was connected to a Downing galvanometer, and the deflections were recorded photographically on a rotating drum.

The iron gas-holder used in Garner and Roffey's apparatus was suspected of not being quite hydrogen-tight, and it was replaced by a five-litre glass bottle; when the pressure in this fell below that required in the bomb, the arrangement of the apparatus permitted the gas to be pumped into the drying-tubes by means of the large gas-burette C (*loc. cit.*,⁷ Fig. 1).

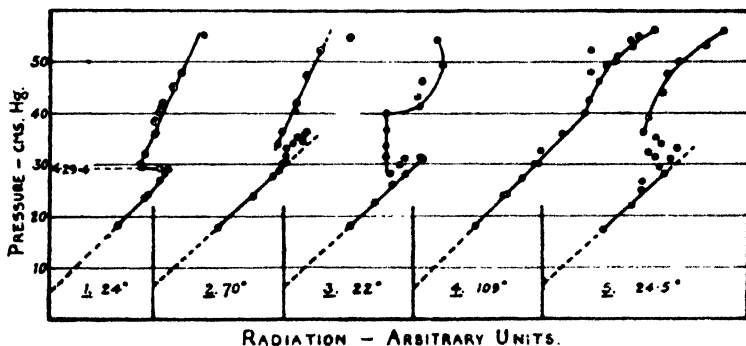


FIG. 1.

The number of P_2O_5 tubes was reduced from five to three, and a liquid-air trap was inserted between them and the bomb. As no difference in the results could be detected whether the liquid-air trap was used or not, for the majority of the experiments only the three P_2O_5 tubes were used for drying the gas. The P_2O_5 had been redistilled in a current of oxygen to remove lower oxides of phosphorus.

The quartz bomb was enclosed in an electric furnace capable of giving any temperature up to 600° C. (*i.e.*, the approximate ignition temperature at the pressures used of the mixture $2CO + O_2$). The bomb was held in position in the furnace by means of two stainless steel rings connected by a spacing-rod about 10 cm. shorter than the bomb, an arrangement which allowed the bomb to be removed and replaced easily. The temperature inside the furnace, which was measured by means of a platinum-iridium thermocouple and a Cambridge Instrument Co. calibrated galvanometer, was constant along the length of the furnace to within 2° C.

A cylindrical copper vessel, through which water could be passed, about 30 cm. diameter and 3 cm. long, was mounted between the furnace and the thermopile to absorb as much as possible of the heat from the furnace; there was a central aperture of about 8 mm. diameter for the passage of the radiation from the bomb. Even with this arrangement, the

⁷ Garner and Roffey, *J.C.S.*, 1929, 1123.

radiation from the hot furnace produced a potential in the thermopile greater than the apparatus could record, and much greater than that produced by the radiation from an explosion. This was overcome by the application, by means of an accumulator and a resistance-box, of a counter-potential across the thermopile such that the zero position of the light on the recording drum was as nearly as possible that of the undeflected galvanometer. This meant that the potential applied to the galvanometer was zero before explosion, and hence that the deflections were proportional to the amount of radiation, as with the cold gas.

The first experiments were done with a new quartz bomb, but after all the preliminary adjustments had been made, a trivial matter of convenience decided that the first series of measurements should be made at a high temperature (190° C.). There seemed to be no *a priori* reason for the temperatures at which the measurements were made following any particular order, and it was hence very surprising to find that after the series at 190° had been done the normal "cold" pressure-radiation curves could no longer be obtained. Washing out the bomb with dilute hydrofluoric acid to remove the surface layers did not restore the conditions to normal. A fresh start was therefore made, using a different bomb. This bomb was one which had been used by Dr. Pollard for gases containing nitrogen peroxide, chlorine, bromine, and iodine, and had given satisfactory curves throughout: it had not previously been heated above room temperature. A series of seven runs was then made with the bomb, starting and ending with two at room temperature and including three at three different elevated temperatures each "sandwiched" in between two at room temperature, *i.e.*, the temperatures for the seven runs were, in order, 24° , 70° , 22° , 109° , 24.5° , 174.5° , 24° .

The results of these experiments are shown in the Fig. Only the curves for the first five series are shown, as no further new features appear in the last two. In every case a mixture containing 0.309 per cent. of hydrogen was used. In drawing the curves, the measured radiation is corrected to that for an equal mass of radiating gas in each case, *i.e.*, it is corrected to a gas temperature of 25° , and to 100 per cent. combustion. A correction was also applied for small variations (of the order of 0.5 per cent.) in the sensitivity of the galvanometer.

Discussion.

Curve 1 is the original curve at room temperature, and is quite normal. The step occurs at 29.4 cm.; 0.309 per cent. of hydrogen corresponds to a partial pressure of 0.091 cm. Substituting 29.4 for p_0 in equation (1), we get a value of 0.094 cm. for the partial pressure of hydrogen.

The effect of raising the temperature of the gas is to increase the pressure at which the step occurs (curves 2 and 4). This proves that of the two hypotheses proposed to account for the step, that of its being a lower ignition limit cannot be correct, so that the only apparent possible alternative explanation, that it is a pressure at which the two mechanisms are equally rapid, is almost certainly the true one.

This increase in p_0 on heating the explosive mixture is precisely the effect which a reduction in the pressure of hydrogen would produce. However, the hypothesis of a more rapid removal of hydrogen by the heated walls can hardly be reconciled with the finding of Garner, Hall, and Harvey,³ that p_0 is unaffected by changes in the diameter of the bomb, which seems to show that a wall effect is not one of the factors determining p_0 . One possible explanation of these apparently conflicting facts is discussed below; another is that the temperature coefficient of

the mechanism operating below the step (mechanism I.) is greater than that of the mechanism operating above the step (mechanism II.). As suggested above, mechanism I. is probably either an oxygen atom chain or a thermal chain, while II. is almost certainly a hydrogen atom chain. Kistiakowsky and Jackson have found that in the case of the photochemical oxidation of carbon monoxide, the rate is independent of temperature in the dry mixture—*i.e.*, the temperature coefficient is zero where hydrogen atom chains cannot occur—while the reaction in the presence of water vapour has a positive temperature coefficient which increases slightly with the temperature.^{8, 9, 10}

Apart from the effect of the temperature on p_s , however, there are some unexpected features in the results. These are:

- (1) The invariance under all conditions of the curves below the step.
- (2) The fact that heating the bomb under a high vacuum * produces changes in the curves subsequently obtained at room temperature, the extent of the change depending roughly on the degree of the preceding heating. The step becomes more diffuse, but remains at about the same pressure and of the same order of magnitude (curves 3 and 5). At the same time, the results at the pressures above the step become erratic.
- (3) The fact that the radiation above the step increases as the temperature of the explosive mixture is raised. Thus, at 45 cm. pressure the radiation is increased by 50 per cent. on raising the temperature from 24° to 109° (curves 1 and 4). This process causes the step to disappear, and at 109° and 174.5° only rather doubtful points of inflexion remain.
- (4) The effects on the percentage combustion. (This was calculated for every explosion from the drop in pressure on re-opening after explosion

Series.	Temperature (°C.).	Average Percentage Combustion.
1	24	94.5 (normal for "cold" explosions).
2	70	96
3	22	88
4	109	90.5
5	24.5	87.5
6	174.5	94
7	24	92

the tap between the bomb and the manometer.) The values obtained tended to rise for the explosions done at the higher temperatures, and to fall again for the explosions done at room temperatures after the bomb had been heated. Some figures for this are given in the table opposite.

In the case of three series done at elevated temperatures (2, 4, 6), there was also a noticeable tendency for the percentage combustion figures to show a large deviation from the mean in the early explosions of each series, and only to settle down to a fairly steady value after eight to ten explosions. The percentage combustion varied a little with the pressure, but not much between 25 and 45 cm., and the explosions at the different pressures were done in a random order. The figures for pressures below 25 cm. are in error by an unknown amount, since at low pressures the flame was

⁸ Kistiakowsky, *Proc. Nat. Acad. Sci.*, 1929, 15, 194.

⁹ Jackson and Kistiakowsky, *J. Amer. C.S.*, 1930, 3471.

¹⁰ Jackson, *J. Amer. C.S.*, 1934, 2631.

* Before doing a series of measurements at a raised temperature, the bomb was always evacuated for at least twelve hours while the furnace was on. The final vacuum was always of the order of 10^{-6} mm. or better, and the evacuation was continued till the increase in pressure over half-an-hour, with the pumps shut off, was negligible.

usually extinguished in the narrow tube leading to the tap. Also, since this tube necessarily projected from the furnace, the gas in the bomb-space was not evenly heated throughout, and although the exact temperature distribution was thus unknown, the percentage combustion at the elevated temperatures was calculated assuming a temperature discontinuity—room temperature to furnace temperature—at the tap by which the gas was admitted to the bomb. To allow, however, for a temperature gradient would tend to increase, if anything, the percentage combustion figures at the higher temperatures, and hence also the differences shown in the table.

These results show that we must distinguish the changes in the reaction occurring at a raised temperature, and those appearing after the reaction vessel has been heated. 1 and 2 show that while mechanism I. is unaffected either by the heating of the walls of the vessel or by any subsequent effects, II. is apparently affected by both to a marked degree. The only explanation for this is that the nature of the surface has been changed, even by so small a rise of temperature as 50° . If it has been rendered in some way unstable, then the step, which represents a delicate equilibrium between the two mechanisms, will cease to be a definite pressure and will become instead a region of pressure throughout which each explosion can leave the surface in a condition to favour either of the two mechanisms. It is clear that changes in the surface could lead to the partial removal of some chain carrier, favouring one mechanism at the expense of the other. Garner and Pollard⁴ have suggested that when the flame is slowed down, *e.g.*, by the presence of chlorine or bromine, the surface, by removing the hydrogen atoms concerned in mechanism II., can affect the completeness of the combustion. A similar explanation could be applied to the results obtained on and after heating, were it not for the objection which arises above, that p_s is unaffected by changes in the diameter of the bomb, indicating that the occurrence of one combustion mechanism rather than the other is not determined by the walls directly. This difficulty vanishes if we assume, firstly, that the walls are normally in such a state (possibly covered with a monomolecular layer of gas) that they cannot, during the rapid passage of a normal flame, adsorb sufficient hydrogen atoms or other chain carriers to affect appreciably the course of the reaction; and secondly, that this condition is removed by heating. This, if true, would provide also an alternative explanation to the one offered above of the positive temperature coefficient of p_s . Steiner^{11, 12} has shown that adsorbed water poisons a glass surface for the heterogeneous recombination of hydrogen atoms; so it is possible that chemically bound water and other impurities are desorbed from the quartz on heating, thus rendering the surface more effective for the removal of hydrogen atoms. Hence the fact, noted under (4), that the percentage combustion figures tend to become less erratic with time, may be explained by a reconditioning of the surface by the adsorption of water, and possibly other substances, after a number of explosions.* The values obtained for the radiation emitted, however, showed no tendency to lie closer to a mean curve after a number of explosions had been done; and there was no apparent connection between large deviations of percentage combustion figures on the one hand, and of amounts of radiation on the other.

* Coslett and Garner,¹³ investigating low pressure CO—O₂ flames in quartz vessels, found that the percentage combustion depended on the state of the surface.

¹¹ Steiner, *Z. physik. Chem., Bodenstein Festsband*, 1931, 817.

¹² Steiner, *Trans. Faraday Soc.*, 1935, 31, 962.

If the above suggestion concerning the state of the surface is correct, then on raising the temperature p_s should no longer remain independent of the diameter of the bomb.

The effects noted in (3) concern the radiation emitted. Bawn and Garner³ found that the amount of radiation emitted above the step depended on the nature of the surface of the vessel, although this had little effect on p_s . The radiation is emitted not only from the flame front, but also from the gases behind, and hence it is more likely to be affected by the nature of the surface than the reaction mechanism in the flame front. The temperature coefficient of the radiation from mechanism II. is therefore probably a surface effect. The amount of radiation emitted from flames containing little or no hydrogen (mechanism I.) is very great, amounting to nearly 25 per cent. of the total heat of reaction.¹⁴ Garner and Johnson have suggested¹⁵ that this high emission is due mainly to chemiluminescence of the freshly formed products, and that on the introduction of hydrogen one of its effects is to deactivate the freshly formed carbon dioxide molecules before they can emit radiation, *i.e.*, it converts their vibrational energy into kinetic energy. This suggestion is supported by the work of Eucken and Becher¹⁶ on the conversion of translational energy of carbon dioxide molecules into vibrational energy. This process is slow for the pure gas, but rapid in the presence of hydrogen or water. The reverse process, vibrational to translational energy, is affected in a like manner. Therefore the increase in the radiant energy emitted by mechanism II. at elevated temperatures could be explained if the deactivation of the newly formed carbon dioxide molecules was less effective at these temperatures. This would mean either that collisions involving carbon dioxide were less effective or that the concentration of the deactivator or deactivators was lower. If hydrogen atoms were the deactivating agent, then their removal by the walls would account for the results obtained. This explanation, however, cannot be other than tentative, as the true cause of the reduction in the radiation emitted on passing from mechanisms I. to II. is still uncertain.

There seems to be no object in adding here to the already voluminous body of discussion on the actual atomic and molecular mechanisms of the carbon monoxide-oxygen explosion.

Summary.

There has been investigated the effect on the radiation emitted on explosion of raising the initial temperature of $a(2\text{CO} + \text{O}_2)$ mixture containing about 0.3 per cent. of hydrogen. It is shown (1) that heating the explosive mixture raises the pressure at which the "step" in the pressure-radiation curve appears, from which the step cannot be a lower ignition limit, and is almost certainly the pressure at which two reaction mechanisms for the flame are equally rapid, and for which two alternative explanations are suggested; and (2) that heating the quartz tube in which the explosion takes place by as little as 50° produces changes in the surface which make the step diffuse. These wall effects are discussed, and are ascribed to the removal of atoms by the walls.

¹³ Coslett and Garner, *Trans. Faraday Soc.*, 1930, **26**, 190.

¹⁴ Hall and Tawada, *Trans. Faraday Soc.*, 1930, **26**, 600.

¹⁵ Garner and Johnson, *J.C.S.*, 1928, 280.

¹⁶ Eucken and Becher, *Z. physik. Chem. B*, 1933, **20**, 467.

In conclusion, the author wishes to acknowledge his extreme indebtedness to the patience and helpfulness of Professor W. E. Garner, who suggested this problem, and to thank the Carnegie Trust for a scholarship, and Messrs. I.C.I. Ltd. for a grant for the purchase of apparatus.

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THE EFFECT OF TEMPERATURE ON THE ABSORPTION OF RESONANCE RADIATION BY SODIUM ATOMS.

BY JAMES L. TUCK AND ERNEST WARHURST.

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The absorption of resonance radiation by sodium atoms has been used by Frommer and Polanyi¹ and by Fairbrother and Warhurst,² as a means of estimating the number of sodium atoms in a given reaction system. In these estimations it has always been assumed that the absorption for a particular radiation was a function of the sodium atom density only. The relationships between the absorption and the number of atoms for various light sources have been published previously (Frommer and Polanyi,¹ Fairbrother and Warhurst,² Fairbrother and Tuck.^{3,4} These absorption curves have all been determined by measuring the absorption in a cell containing sodium in equilibrium with its vapour, both at the same temperature. Hence each point on such curves was taken at a different temperature.

As an addition to the above-mentioned work, the results of some experiments on the variation of absorption with temperature at constant atom density are given below.

Experimental.

The experimental arrangement was exactly as for the measurements of Fairbrother and Tuck,⁴ except for an alteration to the absorption cell. This consisted of the same cell but with the addition of a side-arm projecting from the body of the cell (see Fig. 1). The temperature of the main body of the cell could be varied while the side-arm was maintained at constant temperature.

Difficulties were encountered in early experiments owing to the long time for attainment of equilibrium between the sodium in the side-arm

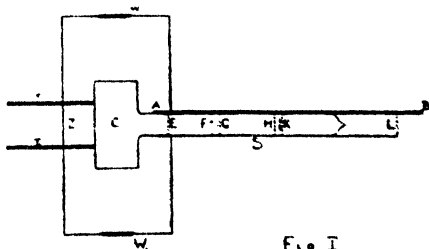


Fig. 1

¹ Frommer and Polanyi, *Trans. Faraday Soc.*, 1934, **30**, 519.

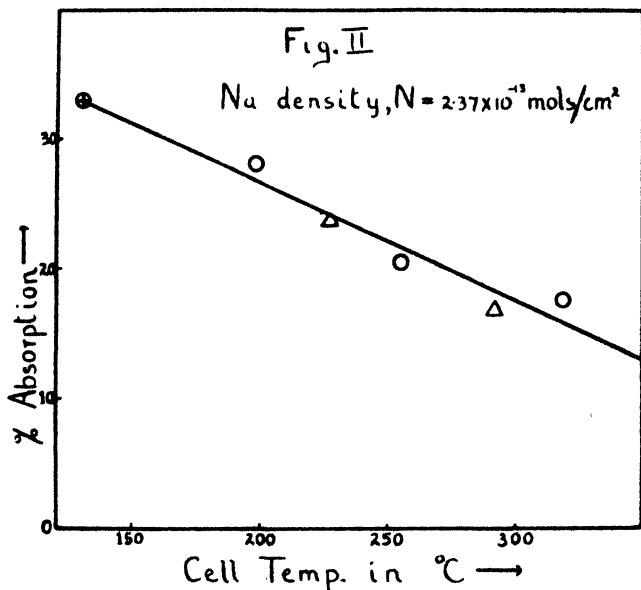
² Fairbrother and Warhurst, *ibid.*, 1935, **31**, 987.

³ Fairbrother and Tuck, *ibid.*, 520.

⁴ *Ibid.*, 1936, **32**, 624.

and the vapour in the main body. This was traced to the presence of residual gas. The difficulty of obtaining sodium free from residual gas is well known, and was overcome by evacuating and outgassing the cell very carefully, the sodium being outgassed by the technique given in the paper of Fairbrother and Tuck.³ A diagram of the cell and heating arrangements is shown in Fig. 1. The main body of the cell, which had plane ends 4.65 cms. apart, was heated in an air-oven Z. The temperature of the cell was taken by two thermometers whose bulbs touched the cell wall. The side-arm was encased in copper foil covered with asbestos paper, over which was wound the heater. AB represents a narrow pyrex tube bound to the side-arm under the copper sheath. By introducing a thermocouple down this tube, the temperature distribution along the side-arm could be explored. For proper control of the sodium and to prevent the higher temperature of C from affecting that of the sodium, the heating of the side-arm was divided into three sections, EF, GH, and HF, the copper sheath underneath being similarly divided.

In an experiment, the main body of the cell C and the sections EF and GH were heated to 300° C. and KL kept cold. These conditions were



maintained for several hours, when GH was cooled; the absorption was found to be independent of the temperature of EF and the main body of the cell. This method of working avoided error due to sodium condensing in zones of intermediate temperature giving false readings of vapour pressure as well as taking a great deal of time for attainment of equilibrium. The readings of the photo-

tronic cell and photoelectric photometer when GH was cold gave the intensities of the incident and transmitted beams respectively and constituted an initial blank.⁴

The side-arm was then adjusted to a uniform constant temperature giving a suitable molar concentration, and the absorption measured for different temperatures of C, time being allowed between each measurement till a steady state was reached. At the end of an experiment KL was cooled and all the sodium distilled into it, as described above. A second blank was then taken which agreed with the first within experimental error.

The difference in temperature between the side-arm and the body of the cell introduces a small change in molar concentration in the main body with change of temperature due to the Knudsen effect. This change was corrected for by assuming the absorption to be proportional to the molar concentrations. This assumption is justified since at the low concentration used in these experiments the curve of absorption against atoms per cm.³ in the beam is almost linear (see Fairbrother and Tuck).⁴

The results are shown graphically in Fig. 2. Percentage absorption is plotted against temperature of the absorbing vapour. The points marked \odot and \triangle correspond to different experiments. The point marked \oplus is taken from the results of Fairbrother and Tuck⁴ and corresponds in our experiments to the cell and side-arm, being at the same temperature. Such a determination would have been difficult in these experiments, as no particular precautions were taken to prevent the condensation of sodium on the plane windows of the cell.

The results show that within experimental error the absorption of a constant number of moles decreases linearly with temperature between 140° C. and 320° C. It is to be understood that the above straight line may not be extrapolated to higher temperatures, since it is obvious that it must be asymptotic to the temperature axis.

The implications of this absorption change, in determinations of velocity constants and activation energies of reactions, by methods in which the number of atoms in a reaction zone ("Flame") is estimated from the absorption, are evident.

Hitherto the absorption by the sodium atoms in a flame has been measured at a flame temperature ranging from 200° to 300° and referred to an absorption curve taken at 110°-180° C. In the new method suggested by Polanyi and communicated in the paper of Fairbrother and Tuck,⁴ future flame work involves the estimation of the number of atoms in a flame by measuring its total absorption. This necessitates using small maximum densities in the flame in order to confine the determinations to the linear part of the absorption curve. The above experiments are for densities in this region and thus provide all the data required for the correction of the linear parts of the curve to any flame temperature up to 320° C. Every point on the straight line (Fig. 2) gives the absorption of 2.37×10^{-13} moles/cm.² at a particular temperature, and since all absorption isotherms are assumed to be linear at this density, this absorption determines the slope of the absorption curve at the particular temperature. The total absorption of a flame at this temperature will hence give directly the number of atoms in it.

A tentative correction may be made of the reaction velocity constants obtained by the old absorption curves (Fairbrother and Warhurst).² Since absorption isotherms must all pass through the point $I_t/I_0 = 1$ for $N = 0$ and approach $I_t/I_0 = 0$ for large N , a method of correcting absorption curves over a big range of absorption may be deduced by applying a cor-

TEMPERATURE : 244° C.

Substance.	Mean Vel. Const. k in cm. ² /mol. secs.	Activation Energy from Collision Yield.
PhCl	2.66×10^{10}	10,200 cal.
PhBr	6.08×10^{12}	4,550 "
PhI	8.90×10^{13}	1,740 "

rection to $\log I_t/I_0$. This method assumes that $\frac{(\log I_t/I_0)_{T_1}}{(\log I_t/I_0)_{T_2}}$ for big N is equal to the experimentally determined ratio at T_1 and T_2 for a small N .

Taking the reaction velocity constants published by Fairbrother and Warhurst² and correcting in the above manner, the results are obtained (see table).

The above figures include a minor correction for the effect of reaction vessel temperature on the carrier gas flow. It is to be emphasized that the absorption correction is of an approximate nature. The constants may be regarded as better approximations to the true velocity constants.

Our best thanks are due to Professor M. Polanyi for his interest in this work and to Dr. Fairbrother for much help and encouragement. We also wish to thank the Department of Scientific and Industrial Research for grants and the Imperial Chemical Industries Ltd. for grants towards the purchase of apparatus.

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CHEMICAL REACTION IN ELECTRIC DISCHARGES. PART I: THE STATISTICAL THEORY OF DISCHARGE REACTION.

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Whilst the facts of chemical reaction in electric discharges show that there is a close connection between the rate of reaction and the electrical conductivity of the gas, there is considerable difference of opinion about the nature of the relationship.¹ So many previously obscure aspects of the conductivity have been elucidated during the last thirteen years² that it now seems profitable to reconsider the problem of this relationship.

The aim of this paper is to show that a statistical treatment of the electron collision processes of the first kind which occur in discharges leads to expressions for the rate of electron collision, and for some other derived quantities, from which it is clear that all these quantities have properties in common with their experimentally determined analogues describing reaction in discharges. If, therefore, such collisions can be shown to constitute the rate determining step in the whole mechanism by which the reaction occurs, quantitative explanation is at once available for the kinetics of discharge reaction. A detailed discussion of individual reactions, which will be given elsewhere, shows that it is usually possible to find a mechanism satisfying these conditions, and that the most frequently occurring case is that in which the first step of the mechanism is a collision between a reactant molecule unaffected by the discharge and a neutral product of an electron collision with such a molecule.

We consider here the cold cathode glow discharge only^{*}; its chemistry and physics have been widely investigated, and other discharge forms are readily related to it. There are two zones only in this form of discharge in which much reaction is known to occur, the negative glow and the positive column (the abbreviations N.G. and P.C. will be used for these). The two experimentally determinable quantities of most interest in connection with the kinetics of discharge reaction are called the current and energy efficiencies; these express the rate of reaction in terms of the

¹ Berthelot, *Essai de Mécanique Chimique*, Paris, 1879, 2; Stark, *Elektrizität in Gasen*, Leipzig, 1902; Löb, *Electrochemie d. organischen Verbindungen*, Halle, 1905; Kirkby, *Phil. Mag.*, 1904, 7, 223; 1905, 9, 171; 1907, 13, 289; *Proc. Roy. Soc., A*, 1911, 85, 151; Tiede and Richter, *Handbuch d. Arbeitsmethoden d. Anorganischen Chemie*, 2, part ii.; Warburg, *Handbuch d. Experimental Physik*, 17; Guntherschulze, *Z. Elektrochem.*, 1924, 30, 637; Finch and others, *Proc. Roy. Soc., A*, 1926, 111, 257; 1927, 116, 529; 1929, 124, 303; 1929, 125, 532; 1930, 129, 656; 1931, 133, 173; 1934, 143, 482; *J.C.S.*, 1935, 32; Lind and others, *Trans. Am. Elec. Chem. Soc.*, 1927, 52, 37; *J.A.C.S.*, 1928, 50, 1767; 1929, 51, 2311, 365; 1930, 52, 4450; *Trans. Am. Elec. Chem. Soc.*, 59, 159, 165; Brewer and others, *J. Physic. Chem.*, 1929, 33, 883; 1930, 34, 153, 554, 1280, 2343; 1931, 35, 1281, 1293; 1932, 36, 2133, 2395; 1933, 37, 889, 897; 1935, 38, 889, 1051; Willey, *Trans. Faraday Soc.*, 1934, 30, 230.

² Darrow, *Electrical Phenomena in Gases*, Baltimore, 1932; Druyvesteyn, *Physica*, 1931, 11, 9.

^{*} Cases in which the current is used mainly for heating the reactants are not considered in this paper.

current carried by the discharge and of the energy supplied to maintain it. The principal characteristics of these efficiencies are as follows. In a given system of reactants the magnitude of either referred to a particular resultant may be widely different in the N.G. and the P.C. Their temperature coefficients are usually very small, and their absolute magnitudes may be considerable in systems where a purely thermal reaction is most unlikely and when the vessel containing the discharge is refrigerated to -180° . Their pressure coefficients are usually very small in the N.G., but may be considerable in the P.C. Their variation with the current density is also very small. Lastly, in a given system of reactants, the products of a discharge may be very different from those of the purely thermal reaction.

1. The Current and Energy Efficiencies of Discharge Reactions.

Although these quantities have been used frequently in describing discharge reactions, it is convenient to restate their definitions, which are slightly different in the N.G. and P.C. because of the physical differences between these zones. For simplicity we consider the usual case of reaction in a cold cathode glow discharge maintained between parallel electrodes in a cylindrical tube of cross-section A cm.² and in which the P.C. occupies a length L cm. The relevant quantities experimentally measurable are:—

- I' the total current carried by the discharge (as measured in the external circuit) in electrons sec.⁻¹
- V_N the potential difference in volts between the cathode and the N.G.
- V_P the potential difference in volts across the P.C.
- $R'_{p,N}$ the rate of formation of reaction product in the N.G. in molecules sec.⁻¹ (the anode is so close to the cathode that the P.C. is suppressed).
- R'_p the rate of formation of reaction product in the whole discharge in molecules sec.⁻¹ (the anode is so far removed from the cathode that a P.C. is present).

The rate of formation of product molecules in the P.C., $R'_{p,P}$, is then given * by $R'_p - R'_{p,N}$. In those regions where the current is carried exclusively by electrons, the current density, I , then follows as $I = I'/A$. In the case of a uniform P.C. the electric field, X , responsible for the transport of the current is then given by $X = V_P/L$, and the volume rate of reaction, $R'_{p,P}$ molecules cm.⁻³ sec.⁻¹, is given by

$$R'_{p,P} = R'_p / (A.L.).$$

In the N.G. the current efficiency, $\beta_{p,N}$, is defined as the number of product molecules formed per unit charge (1 electron) carried by the current, or

$$\beta_{p,N} = R'_{p,N} / I';$$

the energy efficiency, $\eta_{p,N}$, is likewise defined per unit of energy (1 electron-volt) supplied to maintain this zone of the discharge, or

$$\eta_{p,N} = R'_{p,N} / (V_N \cdot I') = \beta_{p,N} / V_N.$$

* This expression for $R'_{p,P}$ assumes the absence of any specific influence of either the anode or the P.C. on reaction in the N.G.

In the uniform P.C. the current efficiency, $\beta_{p,P}$, is defined as the number of product molecules formed per unit volume and per unit current density (1 electron $\text{cm}^{-2} \text{sec}^{-1}$), or *

$$\beta_{p,P} = R_{p,P}/I = R'_{p,P}/(L.I'),$$

from which it will be seen that $\beta_{p,P}$ is numerically equal to the number of product molecules formed per electron of current and per cm. length of the P.C.†, that is, per cm. of electron drift. The energy efficiency, $\eta_{p,P}$, is defined as the number of product molecules formed per electron-volt supplied to maintain this zone of the discharge, or ‡

$$\eta_{p,P} = R'_{p,P}/(V_P . I') = R_{p,P}/(X.I) = \beta_{p,P}/X.$$

2. Expressions for the Rate of Electron Collision.

In the plasma § of a discharge the plasma electrons have a distribution of velocities almost random in direction with a superposed drift in some definite direction which is responsible for the transport of charge, or current, measured in the external circuit. At the junction between a region of space charge and a plasma, or between plasmas of different kinds, the motion of the electrons is more nearly a directed flux with a distribution in velocity.

In the first case, the rate R at which some specified type of collision occurs per cm^3 per sec. between electrons and some specified type of reactant molecule (unchanged by the discharge) is given by §

$$R = k . n_e . \lambda . p \int Q(V) . V^{0.5} . f(V) . dV \quad . \quad . \quad . \quad (3)$$

where λ is the fractional concentration of the specified reactant molecules in a gas at the total pressure p mm. Hg, n_e the concentration of electrons per cm^3 , $Q(V)$ the probability cross-section for the specified type of collision with the specified reactant for an electron of energy V electron-volts, $f(V)$ the electron energy distribution function, and $k = 1.87 \cdot 10^9$ when $Q(V)$ is measured as a multiple of the area of the first Bohr orbit in hydrogen (radius = $0.53 \cdot 10^{-8}$ cm.). In the particular case that the current is carried through the plasma by the drift of the plasma electrons in an electric field X , the collision rate per unit current density, β collisions per cm. of electron drift, is given by

$$\beta = R/(n_e . W) \quad . \quad . \quad . \quad . \quad (4)$$

where W cms. sec^{-1} is the drift speed of the electrons, and the collision rate per unit of energy supplied to the plasma, η collisions per electron-volt, is given by

$$\eta = R/(n_e . W . X) \quad . \quad . \quad . \quad . \quad (5)$$

In order to obtain the corresponding expressions for a reaction product resulting from the initial occurrence of such an electron collision, (3),

* In the case of a non-uniform P.C. the average value of $\beta_{p,P}$ is still given by $R'_{p,P}/(L.I')$, although $R_{p,P}$ may be a function of position.

† This definition was originally given by Kirkby.¹ The quantity usually given in literature is $R'_{p,P}/I' = L . \beta_{p,P}$, which is inconvenient because it depends on L .

‡ In the case of a non-uniform P.C. the average value of $\eta_{p,P}$ is still given by $R'_{p,P}/(V_P . I')$, although $R_{p,P}$ and X may be functions of position.

§ Tonks and Langmuir, *Physic. Rev.*, 1929, **34**, 877.

¶ Fowler, *Statistical Mechanics*, Cambridge, 1928, § 17.

(4), and (5), must be multiplied by a factor ϕ which denotes the number of such product molecules formed per initial electron collision. The factors controlling ϕ are similar to those controlling the quantum yield in reactions initiated by the absorption of light⁵, together with special factors arising only in discharges; an example of the latter occurs when the products of electron collision, or reaction, formed in one zone have to pass through another zone before being isolated. It will be shown in § 4 that, when ϕ is constant, $\phi \cdot \beta$ and $\phi \cdot \eta$ may have many properties in common with the experimentally determinable quantities, $\beta_{p,p}$ and $\eta_{p,p}$.

In the second general case, at the junction between a region of space charge and a plasma, the rate, G , at which some specified type of collision occurs between an electron of a flux entering a plasma and some specified type of reactant molecule (unchanged by the discharge) is given in collisions per sec., by

$$G = I_e \int P(V) \cdot f(V) \cdot dV \quad . \quad . \quad . \quad (6)$$

where I_e is the current in electrons sec.⁻¹ carried by the flux into the plasma, $P(V)$ the total number of collisions of the specified kind effected by an electron of energy V electron-volts before its energy falls too low for it to be able to produce the change in question in the given system of reactants, and $f(V)$ is now the electron energy distribution function for the flux entering the plasma. If the current across the boundary is entirely one of electrons, $I_e = I'$, and the collision rate per unit charge carried by the current, β_f , in collisions per electron, is given by

$$\beta_f = G/I' \quad . \quad . \quad . \quad . \quad (7)$$

and similarly, if V_N is the potential difference necessary to maintain the flux into the plasma, the collision rate per unit of energy supplied, η_f , in collisions per electron-volt, is given by

$$\eta_f = G/(V_N \cdot I') \quad . \quad . \quad . \quad . \quad (8)$$

As in the previous case, the corresponding expressions for the reaction product resulting from the initial occurrence of the specified type of electron collision may be derived by multiplying (6), (7), and (8), by a factor ϕ defined as before. It will be shown in § 5 that, when ϕ is constant, $\phi \cdot \beta_f$ and $\phi \cdot \eta_f$ have again many properties in common with the experimentally determinable quantities for the formation of the reaction product, $\beta_{p,N}$ and $\eta_{p,N}$.

Concerning expressions (3) and (6), it will be noticed that they relate to electron collisions occurring in *the gas phase*, and therefore, if the reactions determining ϕ are homogeneous, it follows that expressions (4), (5), (7) and (8) relate to homogeneous reactions in discharges. The effect of the temperature of the reactants is twofold. Firstly, for given absolute concentrations of reactants, p (as defined on p. 1506) will vary with the temperature; alternatively, if the actual pressure be kept constant, R will tend to diminish as the temperature is increased. On the other hand, G will not vary with temperature on account of the change in the density of the gas because this does not affect $P(V)$. Secondly, the temperature determines the population in the rotational and vibrational states of the reactant molecules, which, in turn, determines the effective value of $Q(V)$ and $P(V)$; but since the range of

⁵ Bonhoeffer and Harteck, *Photochemie*, Leipzig, 1933, p. 183.

temperature concerned in many experiments is both low and small,* the population in the higher vibrational states is in any case negligible and therefore the values of $Q(V)$ and $P(V)$ sensibly constant. Thus, provided the pressure and temperature coefficients of ϕ are small, so are also those of the current and energy efficiencies of reaction as given by expressions (4), (5), (7) and (8).

3. The Chemical Differences between the Positive Column and the Negative Glow.

Since each of these zones is a plasma[‡], the rate of electron collision in each may be discussed in terms of expression (3) from which it may be seen that the magnitude of R is mainly determined by the magnitude of the integral involved. But the magnitude of R in turn determines the value of ϕ . R ; thus, if the attribution of chemical reaction in discharges to electron collisions is correct, the differences in the chemical activity of these two zones are to be sought mainly[†] in terms of the corresponding differences in the value of the integral in (3).[§]

The magnitude of the integral in (3) is mainly determined by the amount of overlap of $Q(V)$ and $f(V)$ considered as functions of V . The form of $Q(V)$ is determined by the type of transition involved.[§] If the transition is allowed optically, $Q(V)$ rises from zero at the critical electron energy to a broad maximum at several times the critical energy, thereafter falling off slowly with further increase in V . If the transition is disallowed optically, $Q(V)$ has a sharp maximum a little above the critical energy. In the N.G., $f(V)$ has a considerable value for $V > \text{ca. } 20$ electron-volts as well as being large for $V < \text{ca. } 5$ electron-volts. In the P.C., $f(V)$ is usually inconsiderable for $V > \text{ca. } 10$ electron-volts. It follows that, in the P.C., reactions initiated by the products of disallowed transitions will be relatively more important compared with reactions initiated by the products of allowed transitions than they are in the N.G. The absolute amount of the former type of reaction may be greater in the N.G. than in the P.C. since n_e attains its maximum value for a given discharge in the N.G. Thus, if in a given system of two reactants, the reaction product resulting from the initial occurrence of a disallowed transition suffered by one reactant is different from that resulting from the initial occurrence of an allowed transition suffered by the other reactant,

* The temperature usually recorded is that of the surroundings of the vessel containing the discharge; this has been varied from -180 to about 200°C.^1 The actual temperature of a gas in which a discharge is passing is difficult to determine, but in many experiments it probably did not exceed that of the surroundings by more than about 100° .

† It is found on evaluating the integral in (3) for typical cases that its value usually has a much greater effect in determining the magnitude of R than have any differences in n_e in the two zones; and, since in many systems it is unlikely that ϕ changes much, this result is independent of small variations in this quantity.

‡ The differences in chemical activity are thus attributed to the same factors that give rise to the differences in the arc spectra in these zones.

§ Whilst there are numerous data for atomic transitions⁶, there are comparatively few for molecular transitions which latter are of the greater importance for discharge reaction. The cases of molecular transitions examined experimentally are found to fall into the same general classifications as do the atomic ones, and since this is to be expected on theoretical grounds⁷ there is no reason to doubt that the similarities between atomic and molecular transitions are not general.

¹ Hanle and Larche, *Ergeb. d. Exakt. Wiss.*, 1931, 10.

⁶ Massey and Mohr, *Proc. Roy. Soc., A*, 1932, 135, 258; Mott and Massey, *The Theory of Atomic Collisions*, Oxford, 1933.

the foregoing considerations predict that the first-mentioned reaction product will be the principal product in the P.C. and that the two products will be formed in the N.G., the second predominating in amount: these considerations thus afford a possible explanation of the dependence of the chemical nature of the product on the zone of the discharge used.* Similarly, if allowed transitions alone are responsible for the formation of a single product in a given system of reactants, the greater overlap of $Q(V)$ and $f(V)$, and the larger value of n_0 , in the N.G. leads to the prediction that the absolute amount of reaction † will tend to be greater in this zone compared with the P.C.: this at once affords a possible explanation of the observed differences between the current and energy efficiencies in these two zones.

4. Reaction in the Positive Column.

The uniform P.C. is a plasma ‡ to which the expressions (3), (4), and (5) are applicable. It is nevertheless not possible to predict from these expressions with certainty any general rules for the dependence of the quantities R , β , and η , on p and X . Furthermore, in considering the corresponding (theoretical) quantities for reaction, it may be noticed that, even if λ is constant, ϕ itself may be a function of p , and of the radius of the tube in which the discharge occurs, if a significant part of the reaction occurs on the walls of the tube, because these quantities will determine the rate at which the primary products of electron collision will diffuse to the walls.

Since many discharge reactions appear to be homogeneous§, we shall consider this special case and assume in addition that ϕ is constant, and that λ is constant (this being attainable with comparative ease in

* The simplest case known is a system of one reactant, helium. The formation of triplet He_2 molecules as the main product of reaction is detectable in the P.C.: the formation of such molecules can arise only as the consequence of the initial occurrence of a disallowed transition, since the ground state of helium atoms is singlet (the triplet molecule of lowest energy is derived from the combination of a 1^1S with a 2^3S atom). In the N.G. the formation of both singlet and triplet molecules in comparable amounts is detectable: the formation of singlet molecules arises as the consequence of the initial occurrence of an allowed transition (the lowest stable singlet molecule is derived from the combination of a 1^1S with a 2^1S atom, the latter being formed mainly by emission of radiation from 3^1P atoms).⁶

† Emeléus, Cowan and Brown, *Nature*, 1931, 127, 593; Cowan, *Thesis*, Belfast, 1931; Keyston, *Phil. Mag.*, 1933, 15, 1162; Emeléus and Duffendack, *Physic. Rev.*, 1933, 44, 322.

‡ In discussing the absolute amount of reaction, it is necessary to bear in mind (*cf.* the definitions in § 1) the importance of making due allowance for the length of the P.C. which may be extended indefinitely by separating the electrodes and correspondingly increasing the potential between them.

§ In an actual discharge tube the P.C., itself a plasma, is separated from the walls by a thin sheath of space charge⁷: the thickness of this annulus of space charge is negligible compared with the diameter of the P.C., which fills the remainder of the tube, for the range of pressures and tube diameters which are generally used for examining reaction in glow discharges. The expressions (3), (4), and (5), relate strictly speaking, to the isotropic region forming the main bulk of the P.C., but at its boundary by the sheath and by the Faraday dark space at its "head" the conditions may be different: however, since the volume occupied by the boundary regions is (usually) inconsiderable compared with the isotropic region, it is a good approximation to consider the whole volume enclosed by the discharge tube (over the length of the P.C.) as an isotropic region of plasma.

§ There is very little evidence for the existence of heterogeneous discharge reactions.

experiment). From (3), (4), and (5) it follows that the current and energy efficiencies for the formation of a single reaction product resulting from a single electron collision process may be expressed by

$$\phi \cdot \beta \cdot p^{-1} = k \cdot \lambda \cdot W^{-1} \cdot I(V) \quad (4.1)$$

and
$$\phi \cdot \eta = k \cdot \lambda \cdot (W \cdot Xp^{-1})^{-1} \cdot I(V) \quad (5.1)$$

where $I(V)$ is the integral in (3). In the particular case that $f(V)$ does not change with X and p , $I(V)$ may be replaced by another function, $I_1(\bar{V})$, where \bar{V} is the average electron energy, because $f(V)$ may then be replaced by another function $f_1(\bar{V})$. For very low current densities \bar{V} and W are known, for a given gas, to be functions of Xp^{-1} only⁹; reasons for believing that this dependence extends to the higher current densities of P.C. discharges have been discussed by Townsend⁹, and have been elaborated recently by Lunt and Meek.¹⁰ When V and W depend only on Xp^{-1} it follows that $I_1(\bar{V})$ depends on Xp^{-1} only, and therefore, when λ is a constant, that $\phi \cdot \beta p^{-1}$ and $\phi \cdot \eta$ are functions of Xp^{-1} only; moreover when ϕ , λ , $Q(V)$, and the form of the electron energy distribution function are known, the absolute values of $\phi \cdot \beta p^{-1}$ and $\phi \cdot \eta$ may be calculated from (4.1) and (5.1) as functions of Xp^{-1} . Since in a given gas Xp^{-1} depends mainly on p over a wide range of current density (for a given diameter of discharge tube), it follows that $\phi \cdot \beta$ and $\phi \cdot \eta$ will vary with the pressure but be independent of the current density over a wide range: expressions (4.1) and (5.1) thus provide a possible explanation of experimentally observed properties of the current and energy efficiencies in the P.C.* The explanation becomes definite when the initial type of electron collision is identified, when it can be shown that a reaction mechanism exists in which the initial and rate determining step is the reaction between the product (or products) of the particular electron collisions and reactant molecules unchanged by the discharge, and which is consistent with the postulated constancy of ϕ , and when it can be shown that the (theoretically) calculated dependence of $\phi \cdot \beta p^{-1}$ and $\phi \cdot \eta$ on Xp^{-1} is in quantitative agreement with the experimentally observed dependence of $\beta_{p,p} \cdot p^{-1}$ and $\eta_{p,p}$ on Xp^{-1} . It will be seen that even by the introduction of simplifying conditions no general conclusion can be reached concerning the identification of the type of electron collision the product of which initiates reaction: it is necessary to examine the theoretical and experimental data in detail in any given system of reactants before a conclusion can be reached.

In a striated P.C. the conditions are more complex.³ At the head of a striation, where a directed electron flux rapidly degenerates into an almost random motion, either expression (3) or (6) may be used as in the N.G.† The head of the P.C. in this respect is similar to the head of a striation.

⁹ Townsend, *Electricity in Gases*, Oxford, 1915; *The Motion of Electrons in Gases*, Oxford, 1925.

¹⁰ Lunt and Meek, *Ionisation, Excitation, and Chemical Reaction in Uniform Electric Fields*, Part II. (*Proc. Roy. Soc.*), in the press.

* It is noteworthy that the first observation of the dependence of the experimentally determined quantity, $\beta_{p,p} \cdot p^{-1}$ on Xp^{-1} was made by Kirkby¹ when examining the formation of water from electrolytic gas; a further examination of his data shows that $\eta_{p,p}$ was also dependent on Xp^{-1} only, and over a considerable range of current density.

† Cf. footnote *, p. 1511.

5. Reaction in the Negative Glow.

Although this zone is also a plasma ² it is not practicable to discuss the theoretical quantities derived for reaction in terms of the expressions (4) and (5) because in this zone the current is carried mainly by the diffusion of electrons and not by the drift due to a field; it is, therefore, convenient to discuss this zone in relation to expressions (6), (7), and (8).^{*} Since the field in this zone is negligibly small, there is little motion of ions or electrons across the cathode dark space—N.G. boundary except that associated with the flux of electrons from the cathode dark space, and I_e is therefore sensibly equal to I' ; for the same reason the whole energy available in the N.G. is that brought in by the flux, this is about one-sixth of the total energy supplied externally to maintain the region of the discharge extending from the cathode to the N.G. (and Faraday dark space).¹¹ Of this fraction only that part can be used for effecting excitation processes which is left over after the ionisation processes necessary to maintain the N.G. have been allowed for; this limits the amount of reaction initiated by the products of excitation processes which can occur.

For the reasons stated in the previous section we shall again consider the simple conditions arising when λ and ϕ are constant. If the cathode fall in potential is normal, V_N , $f(V)$ in (6) has then average ¹¹ value $\bar{V} = \text{ca. } V_N/6$, and is zero for $V > \text{ca. } V_N$, independent of the pressure; $f(V)$ can thus vary little if at all with the pressure. Provided that the composition of the gas is constant, and that the dimensions of the N.G. are large compared with the electron mean free path, $P(V)$ is also constant independent of the pressure since it is determined only by the number of collisions which an electron makes before its energy falls below the critical for the specified process. The integral in (6) is therefore practically independent of the pressure and G is proportional to I' . It then follows from (7) and (8) that $\phi \cdot \beta_r$ and $\phi \cdot \eta_r$ for the formation of a single product resulting from a single electron collision process are likewise independent of the pressure and the current density: expressions (7) and (8) thus provide a possible explanation of the observed properties of the current and energy efficiencies in the N.G.† The conditions under which the explanation becomes definite are now essentially the same as those stated when discussing the analogous case of reaction in the P.C. (cf. p. 1510), except that it is now necessary to show that the values of $\phi \cdot \beta_r$ and $\phi \cdot \beta_f$ calculated from (7) and (8) ‡ are in quantitative agreement with the experimentally determined quantities, $\beta_{p,N}$ and $\eta_{p,N}$.

When the cathode fall in potential is abnormal, V_N , the average value of $f(V)$ will still occur ¹¹ at about $V_N/6$, but since $V_N' > V_N$, and V_N varies with I' , G/I' will no longer be necessarily independent

^{*} In the N.G., even when λ is constant, all the quantities in expression (3) for R , except $Q(V)$, may be functions of position. Since the actual rate of collision must be independent of any postulated mechanism by which its algebraical expression is derived, it follows that the integral of R throughout the volume through which the N.G. extends must be equal to G , as given by expression (6).

¹¹ Guntherschulze, *Z. Physik*, 1924, **23**, 334; Linder, *Physic. Rev.*, 1931, **38**, 679; Emeleús and Kennedy, *Phil. Mag.*, 1934, **18**, 874.

† Again it is interesting to note that first observations of the experimentally determined quantities, $\beta_{p,N}$ and $\eta_{p,N}$ were made by Kirkby.¹

‡ The numerical evaluation of the integral in (6) is at present restricted to ionisation processes because for these alone ¹² are data available for $P(V)$.

¹² Langmuir and Jones, *Physic. Rev.*, 1928, **31**, 402.

of the cathode fall in potential although it will independent of the pressure if V_N is constant (*i.e.*, I' constant). It is sometimes found that $\beta_{p,N}$ is constant although V_N is varying.* Since $P(V)$ increases with V , this implies that less of the current carried across the boundary between the cathode dark space and the N.G. may be carried by fast electrons, and more by positive ions, as V_N increases; for this possibility there is independent evidence.¹³

6. Reaction in Other Discharge Zones.

Little attention has been paid to reaction in the cathode glow or in the Faraday dark space, but they have interesting possibilities. Spectroscopic study¹⁴ of the cathode glow has shown that it may contain neutral atoms or molecular fragments of unusual types. The possibility exists of separating and utilising these in quantities approaching those which would be obtained if each, when charged, was responsible for the whole transport of current between the cathode and the cathode dark space. The Faraday dark space often has peculiar properties because of the presence of metastable atoms^{2, 3, 15}; it is possible that some reactions attributed to the N.G. would be more correctly described as occurring in the contiguous parts of the Faraday dark space.

Summary.

The statistical theory of electron collision processes of the first kind has been developed with particular reference to the conditions found in the negative glow and the positive column. This leads to expressions for the current and energy efficiencies of such processes which show that these quantities have the properties frequently exhibited by the corresponding efficiencies for chemical reaction in these zones of a glow discharge. The nature of the relationship between the corresponding efficiencies is outlined.

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* From § 1 it will be seen that $\eta_{p,N}$ is then *not* constant.

¹³ Emeléus, Brown and Cowan, *Phil. Mag.*, 1934, **17**, 146.

¹⁴ Emeléus and Hall, *Proc. Roy. Irish Acad., A*, 1931, **40**, 1; Harkins and Jackson, *J. Chem. Physics*, 1933, **1**, 37.

¹⁵ Emeléus and Duffendack, *Physic. Rev.*, 1933, **44**, 322.

MAGNETIC SUSCEPTIBILITY OF BINARY ALLOYS OF THALLIUM.

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The mass susceptibility has frequently been shown to be an excellent property for the investigation of the nature of alloys, in particular the measurement of this property will indicate the existence of intermetallic compounds, change of allotropic state and change of crystalline form of the constituents of an alloy. With the object of investigating the nature

of the binary alloys of thallium, the variation of the mass susceptibility with change of composition has been measured for complete series of alloys of this metal with cadmium and bismuth, respectively. The measurements have been made with specimens of the alloys, both freshly cast and annealed in a vacuum at a temperature somewhat below the melting-point of the alloy. The measurement of the annealed specimens was undertaken because of a criticism by Shimizu¹ of some measurements of Spencer and John,² in which it is claimed that the divergence in the values of the two sets of measurements is due to absorbed gases in the specimens of the latter authors.

Materials.

The bismuth and cadmium (Kahlbaum) were the purest obtainable. Analysis of the material confirmed this. The thallium on analysis was found to contain appreciable quantities of lead and bismuth, and it was purified before use. The metal was dissolved in dilute sulphuric acid, the solution filtered and allowed to crystallise. The thallium sulphate was twice recrystallised from water. The recrystallised material in about 5 per cent. solution was made slightly acid with sulphuric acid and treated with hydrogen sulphide until there was no further precipitation of lead and bismuth sulphides. The solution was filtered and boiled to remove hydrogen sulphide, and when cold electrolysed in a large flat dish using platinum electrodes, the anode being enclosed in a small porous pot to prevent the metal becoming contaminated with thallic hydroxide, which was formed in small quantities at the anode. The metal was collected and repeatedly washed with air-free water and preserved under air-free water until required. The purified metal was shown to contain less than 1.4 parts of bismuth in 10 million parts of thallium by the cinchonine-potassium iodide reaction,³ and less than 0.8 parts of lead per million by the diphenyl thiocarbazon (dithizone) reaction.⁴ All three metals were examined for the presence of iron by the thioglycollic acid reaction⁵ and shown to contain less than one part of iron in 10 million parts of the metal.

Preparations and Analysis of Specimens.

The alloys were cast into sticks about 9 cms. long and 0.68 cms. diameter. The metals in approximately the required proportions were melted in a graphite crucible and stirred with a silica rod. Owing to the ease with which molten thallium oxidises in air, it was found necessary, in the case of all alloys containing more than 50 per cent. of thallium to prepare the sticks in an atmosphere of nitrogen. The molten metal was poured into carbon moulds of the required diameter. After cooling the sticks of metal could generally be pushed out of the mould, because of the contraction of the alloys on solidification, in other cases the mould had to be broken to obtain the rod of alloy. The sticks of metal were rubbed with fine sand paper until they would slide easily into the measuring tubes, and then washed successively with diluted hydrochloric acid and water to remove traces of iron which may have become attached to the surface. The sticks were dried with absorbent paper and placed in a desiccator and dried over sulphuric acid in a vacuum. The sticks were then cut to a length 7.4 cms. by removing pieces from both ends, which were used for analysis. The end portions were separately dissolved in acid, tested for iron by the thioglycollic acid reaction and the solution used for the deter-

¹ Shimizu, *Sc. Rep. Tohoku Imp. Univ. Series 1*, 1932, **21**, 826.

² Spencer and John, *Proc. Roy. Soc. A*, 1927, **116**, 61.

³ Leger, *Z. anal. Chem.*, 1889, **28**. Feigl and Neuber, *ibid.*, 1923, **62**.

⁴ Fischer, *Wiss. Veroff. Siemens Konz.*, 1925, **4**, 159. *Microchem.*, 1930, **8**, 319.

⁵ Lyons, *J. Amer. Chem. Soc.*, 1916, **49**, 1927.

mination of the thallium content. In no case was iron detected. The thallium was determined by adding a solution of sodium carbonate to the boiling solution of the alloy, on continued boiling the whole of the cadmium and bismuth was precipitated as basic carbonate. The solution was cooled, filtered and washed with boiling water until the filtrate gave no reaction with potassium iodide solution. In the case of the cadmium alloys a 2 per cent. solution of sodium carbonate was used for washing, since hot water alone tended to peptise the basic carbonate. The filtrate and washings were brought to about 300 c.c., raised to the boiling point, and 2 grms. of finely powdered potassium chromate added for every 100 c.c. of solution. The precipitate of thallous chromate was left to settle overnight and filtered on a sintered glass crucible, washed successively with 2 per cent. potassium chromate and 50 per cent. alcohol, dried at 120° C. and weighed. The method of analysis adopted was compared with the iodide method, when it was shown the results of the chromate method were the more reliable, and almost 0.1 per cent. higher than those from the iodide method. The two ends of a stick of alloy almost invariably had an identical thallium content. No rod was used for magnetic measurement if a variation of more than 0.1 per cent. existed between the composition of the ends. The mean composition of the end pieces was taken as the composition of the alloy under measurement.

The whole of the cadmium-thallium alloys were tough and contracted on solidification, those with a high cadmium content were bright and had a silver lustre, whilst those with a high thallium content were lead-like in appearance. Bismuth-thallium alloys with a low thallium content were brittle and had a silver lustre, whilst with a thallium content above 40 per cent. the alloys were less brittle and contracted very much on solidification, they were dull in appearance and oxidised in air more rapidly the higher the thallium content.

Measurement of Susceptibility.

The mass susceptibility measurements were made at room temperature (21°-23° C.) by the modified Gouy method, as described by Sugden⁶ and Trew and Watkins,⁷ using a field strength of about 5000 gauss. Five individual measurements were made of the pull of the field on the specimen and the mean of the five values, which did not vary by more than the experimental error of the method, accepted as the pull of the field on the specimen. From this value, the mass susceptibility was calculated in the usual way. The results, which may be taken as accurate to within 1.0 per cent., are recorded in the tables below. Table I. gives the mass suscepti-

TABLE I.— $-\chi \times 10^{-6}$.

David and Spencer.		Honda*.	Owen.†	Shimizu.‡
Cd . .	0.163	0.18	0.18	0.16
Bi . .	1.292	1.38	—	1.39
	1.320 annealed			
Tl . .	0.223	0.23	—	—

* *Loc. cit.*⁶

† *Ann. Physik*, 1912, **37**, 657.

‡ *Loc. cit.*¹

bility of the pure metals together with such values as are to be found in the literature. Table II. gives the data for the thallium-bismuth alloys, the thallium content of the alloy in weight and atoms per cent. is recorded in the first two columns, whilst columns 3 and 4 give the mass susceptibility

⁶ Sugden, *Trans. Chem. Soc.*, 1932, 161.

⁷ Trew and Watkins, *Trans. Faraday Soc.*, 1933, **29**, 1310.

in the usual units for the unannealed and annealed alloys respectively. Table III. gives the same details for the thallium-cadmium alloys.

TABLE II.

	Weight Per Cent. Tl.	Atoms Per Cent. Tl.	$-\chi \times 10^{-6}$.	$-\chi \times 10^{-6}$ Annealed.
Pure Bi	0.0	0.0	1.292	1.320
Alloy A	7.34	7.50	0.996	1.010
" B	21.15	21.53	0.451	0.451
" C	25.39	25.80	0.288	0.304
" D	30.80	31.22	0.133	0.137
" E	34.50	35.00	0.090	0.090
" F	39.42	40.37	0.145	0.147
" G	47.04	47.60	0.150	0.147
" H	54.85	55.42	0.138	0.125
" I	62.49	63.01	0.114	0.110
" J	70.62	71.09	0.059	0.054
" K	76.92	77.34	0.117	0.112
" L	81.14	81.41	0.110	0.114
" M	92.41	92.58	0.161	0.159
Pure Tl	100.00	100.00	0.223	—

TABLE III.

	Weight Per Cent. Tl.	Atoms Per Cent. Tl.	$-\chi \times 10^{-6}$.	$\chi \times 10^{-6}$ Annealed.
Pure Cd	0.00	0.00	0.163	—
Alloy A	13.49	7.91	0.174	—
" B	19.33	11.69	0.178	0.182
" C	33.40	21.65	0.192	—
" D	41.94	28.47	0.194	—
" E	51.14	36.57	0.196	—
" F	60.14	45.40	0.198	—
" G	70.58	50.94	0.200	—
" H	79.41	68.22	0.216	0.223
" I	87.49	79.43	0.220	—
Pure Tl	100.00	100.00	0.223	—

Discussion.

The mass susceptibilities of the pure metals are in general agreement with the values obtained by previous workers. The values given by Honda⁸ were corrected for a small iron content, whilst in the present work the specimens measured did not contain an amount of iron which would affect the value obtained, and consequently the values recorded were not rendered uncertain by the application of a rather indefinite correction. The susceptibility-composition-curve for the bismuth-thallium alloys shows definite maxima at points corresponding with alloys containing 36 and 71 per cent. of thallium respectively. These compositions are those of intermetallic compounds Bi_2Tl_3 and Bi_3Tl_2 , respectively. The existence of these compounds is also indicated by the work of Medenhall and Lent.⁹ The freezing-point composition curve obtained

⁸ Honda, *Ann. de Physik*, 1910, **32**, 1027.

⁹ Medenhall and Lent, *Physic. Review*, 1911, **32**, 406.

by Heycock and Neville¹⁰ indicates the existence of Bi_3Tl_3 , and these authors isolated the compound as a soft malleable mass melting at 211.7°C . Freezing-point curves furnish no evidence of the existence of Bi_3Tl_3 , but they indicate Tl_3Bi with a transition point at 90°C . On the other hand, E.M.F. measurements of cells with bismuth-thallium alloys as electrodes, made by Kremann and Löbinger,¹¹ as well as a study of the thermal expansion by Omodei and an investigation of the thermoelectric properties by van Aubel¹² all furnish evidence of the existence of both the tri- and penta-bismuthide of thallium. The electroconductance experiments of Geuther and Shultze¹³ support the evidence for the existence of Bi_3Tl_3 , but offer no confirmation for the existence of BiTl_3 , although they suggest BiTl_3 . The difference between the mass susceptibility of the annealed and unannealed specimens of the bismuth-thallium alloys is quite irregular and not very large, the greatest change being about 12 per cent., whilst in many cases it does not exceed the amount of the probable experimental error of the measurement. A peculiar feature of the results lies in the fact that alloys containing less than 40 per cent. of thallium are more diamagnetic after annealing than before, whilst alloys containing more than 40 per cent. of thallium, with one exception, are less diamagnetic after annealing. Whilst the change in the susceptibility of alloys with less than 40 per cent. of thallium could be due to the removal of adsorbed oxygen, this is unlikely owing to the ease with which thallium combines with oxygen, the change in the alloys containing a higher content of thallium must be due to some other cause which is not apparent. The susceptibility-composition curve for the thallium-cadmium alloys shows no irregularities, so that it may be taken such alloys are mixtures of the constituent metals, and they have mass susceptibilities which can be calculated from the mixture law. A search of the literature furnishes no evidence at variance with this conclusion, there being no evidence to support the existence of any intermetallic compound of these metals. It was found impossible to get values for the annealed thallium-cadmium alloys which would be exactly comparable with the values for the unannealed alloys, for cadmium volatilised appreciably during the annealing. One or two values were measured, and are included in the table. These were obtained by calculating the susceptibility after the loss of weight and the change in composition had been evaluated.

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¹⁰ Heycock and Neville, *Trans. Chem. Soc.*, 1892, **61**, 888; *ibid.*, 1894, **65**, 31.
65.

¹¹ Kremann and Löbinger, *Int. Z. Metallog.*, 1920, **12**, 246.

¹² van Aubel, *Bull. Acad. Belg.* (5), 1926, **12**, 559.

¹³ Geuther and Shultze, *Z. Physik.*, 1923, 1106.

A NOTE ON THE ABSORPTION SPECTRUM OF CHLORINE.

By C. F. GOODEVE AND B. A. STEPHENS.

Received 21st July, 1936.

The measurements by Halban and Siedentopf¹ of the extinction coefficient curve of chlorine show a sudden rise between 579 $m\mu$ and 614 $m\mu$, followed by a slight diminution. A total increase of over one-hundredfold was recorded, with a maximum value of the extinction coefficient at 614 $m\mu$ of 0.049 (the concentration is expressed in mols. per litre, length in cms. and the logarithms of intensities to the base 10). It would seem from these observations that a new band system appears in the red, arising from a combination with some intermediate electronic state.

We have examined the absorption of 3355 cms. layers² of cylinder chlorine at pressures up to two atmospheres and at wavelengths between the limit of the normal band system (about 600 $m\mu$) and the limit of the infra-red photographic plates (about 1150 $m\mu$). A Hilger Constant Deviation spectrograph was used. (Dispersion (6000 Å.) = 70 Å. per mm.)

No absorption was found in this region despite the fact that extinctions as low as 5×10^{-4} have been measured. It would appear, therefore, that the absorption found by Halban and Siedentopf, was due to the presence of an impurity or to an experimental error.

The normal band system of chlorine ($O^+ \leftarrow {}^1\Sigma^+_g$) has been investigated by a number of authors and an assignment of quantum numbers has been made by Elliott.³ An analysis by Birge⁴ led him (no data given) to the conclusion that Elliott's vibrational quantum numbers for the upper state, should be reduced by two. A complete assignment based on this analysis is given by Weizel.⁵

With the above large optical thickness of chlorine, it was possible to find additional

TABLE.* — THE WAVE-NUMBERS OF THE EXTREME BANDS OF CHLORINE.

ν''	2.	3.
1.	17,270 (17,300)	16,729 (16,770)
2.	17,498.6 17,500 17,495.4	16,957 16,950
3.	17,694.6 17,700 17,701.9	17,153.9 17,160
4.	17,891 17,893.9	17,350.3 17,360 17,352.1
5.	18,071 18,088.8	17,530 17,540 17,536.5
6.	18,261.8	17,707.0

* Heavy type — present measurements. Light type — Elliott's measurements — Italics — calculated from Weizel's equation.

¹ H. von Halban and K. Siedentopf, *Z. physik. Chem.*, 1923, 103, 71.

² For a description of the apparatus see, C. F. Goodeve and A. W. C. Taylor, *Proc. Roy. Soc., A*, 1935, 152, 221.

³ A. Elliott, *Proc. Roy. Soc., A*, 1930, 127, 638.

⁴ R. T. Birge, *Physic. Rev.*, 1930, 35, 133.

⁵ *Handbuch der Experimentalphysik, Bandenspectren-Band*, by Weizel, 1931, p. 376.

members of the series, the extinction coefficients of which are very low. The wave numbers of the observed band heads are shown in the table. These bands fit, without difficulty, into the scheme of assignment as given by Birge and Weizel, part of which is shown. It is to be noted that the quantum number of the lowest vibration level of the upper state found in absorption, is 1. The extinction coefficient at the maximum of the corresponding two bands is about 5×10^{-4} , while that of the next two ($\nu' = 2$), is about 10^{-3} (the positions of the heads of these bands were difficult to determine). These values are higher than those found by Halban and Siedentopf for this range. It may be that an increase in tube length or in pressure would bring out further members of the series, but difficulties were encountered due to the absorption by minute traces of iodine. The dispersion was not sufficiently high to detect the isotope shift and the results offer, therefore, no further evidence as to the *exact* assignment of quantum numbers to the upper state, except in so far as they eliminate the possibility of the present assignment being more than one unit too high.

THE ABSORPTION SPECTRUM OF CHLORINE HEPTOXIDE.

By C. F. GOODEVE AND B. A. M. WINDSOR.

Received 21st July, 1936.

The anhydride of perchloric acid, Cl_2O_7 , was first isolated by Michael and Conn¹ and described by them as a "colourless oil." Its absorption spectrum has now been examined and approximate extinction coefficients determined.

Liquid heptoxide was prepared and purified² and condensed in a trap attached to a 30 cm. quartz absorption cell and a modified Bodenstein quartz spiral manometer.³ Light from a hydrogen discharge tube passed through the absorption cell into a Hilger small quartz-spectrograph, E. 37. Spectrum photographs were taken at different pressures (different temperatures of the trap), and blanks were taken with different times of exposure.

At the highest pressure used, 85 mm., the heptoxide vapour was found to be completely transparent as far as about 3000 Å. Below this wave-length a smooth continuous absorption band set in and increased in intensity as far as could be measured, 2000 Å. No maximum was found.

In order to determine the approximate extinction coefficients microphotometer tracings were made for each exposure and compared with the blanks. The extinction coefficients, α and ϵ , have been calculated from the equation

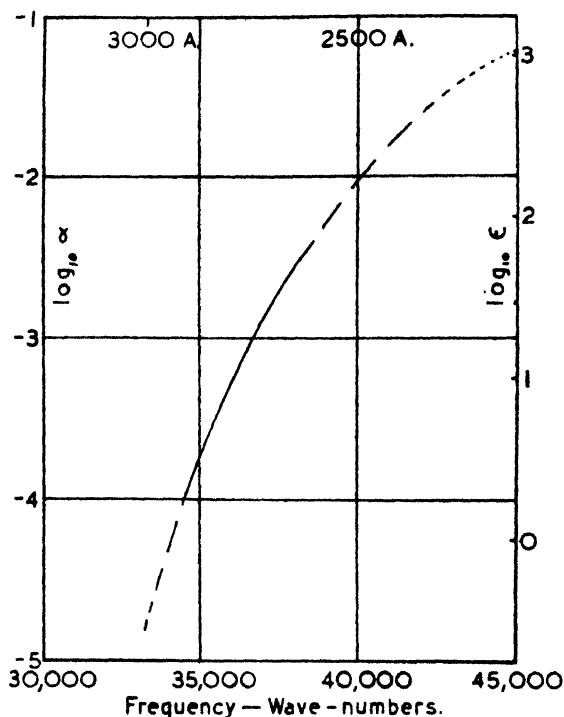
$$\log_{10} \frac{I_0}{I_T} = \alpha pl = \epsilon cl,$$

¹ A. Michael and W. T. Conn, *Amer. Chem. J.*, 1900, **23**, 444.

² C. F. Goodeve and J. Powney, *J. Chem. Soc.*, 1932, 2078.

³ Janet W. Goodeve, *Trans. Faraday Soc.*, 1934, **30**, 501.

where the pressure p is in mm. Hg., the length l in cm., and the concentration c in gram molecules per litre. The tracings gave overlapping sections of the extinction coefficient curve and have been fitted together into the curve shown in the Figure (the logarithms of the coefficients are plotted). In the central part of the curve the absolute values of $\log \alpha$ may be in error by as much as ± 0.1 owing to variation in the blanks, but the relative values are probably more accurate than this. In the regions of high and of low density of the photographic plate the limits of error are however higher. The curve for these regions is indicated in the Figure by a broken line.



The absorption spectrum of
chlorine heptoxide.

There is an interesting parallelism between the absorption spectra of the oxides of chlorine and of nitrogen. The mon-oxides of both show regions of continuous absorption.^{4,5} Both the dioxides have a complex band system in the visible and near ultra-violet. The oxide of nitrogen corresponding to Cl_2O_7 is N_2O_5 . The absorption of the latter is continuous,⁶ commencing also at about 3000 Å. and extending into the far ultra-violet.

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University College, London.*

⁴ Cl_2O . C. F. Goodeve and Janet I. Wallace, *Trans. Faraday Soc.*, 1930, **26**, 254.

⁵ N_2O . L. Henry, *Compt. rend.*, 1935, **200**, 656, and others.

⁶ H. C. Urey, L. H. Dawsey and F. O. Rice, *J.A.C.S.*, 1929, **51**, 3190.

REVIEWS OF BOOKS.

Solubility of Non-Electrolytes. By JOEL H. HILDEBRAND. American Chemical Society Monograph. New York: Reinhold Publishing Co.; London: Chapman and Hall, Ltd., 1936. Pp. 199 (including title page and general preliminaries). Price 22s. 6d. net.

The second edition of this book has been largely rewritten in view of the accumulation of experimental data and of theories of dipole moments, intermolecular forces and non-ideal solutions since the first edition. The study is introduced by a general discussion of deviations from the laws of ideal solutions as based on Raoult's law and the Gibbs-Duhem equation, particular attention being paid to the effects of molecular volumes. A brief discussion of polarity includes Langmuir's theory of surface energies. The forces between non-polar molecules are discussed on the basis of modern quantum theory. A number of special problems, such as solvation, association, vapour pressures, solubilities, metallic solutions and partition, are discussed, ample experimental material and good applications of modern theory being introduced. The book handles a large range of topics with marked originality and success and is likely to prove as stimulating as the first edition was in its time. The price is high.

J. R. P.

The Structure of Metals and Alloys. By WILLIAM HUME-ROTHERY. (Institute of Metals Monograph and Report Series No. 1. Pp. 120 + 60 Figs. 3s. 6d.)

The series of monographs which the Institute of Metals intends to publish from time to time has made a good beginning with Dr. Hume-Rothery's survey of the structure of metals and alloys, which will interest many others than metallurgists. The new conceptions concerning equilibria in solid systems have so greatly altered the way of considering alloys and their transformations that metallurgists who have not followed closely the recent developments may well feel somewhat lost. This monograph, which does not deal with experimental methods, provides a compact and attractive survey of a difficult field. It is self-contained, beginning with an account of the electronic structure of atoms, molecules, and crystals, and passing to the crystal structure of the elements, typical lattices being figured and explained. A discussion of the atomic radii of the elements follows, the uses and limitations of Goldschmidt's values being clearly indicated. The next sections show the influence of the author's own work, a very full account being given of the effects of atomic diameter and of electronic constitution on solid solubility and on the form of the liquidus and solidus curves. Although some of the relations found must still be regarded as empirical, they have undoubtedly brought some degree of order into the puzzling diversity of the equilibrium diagrams of alloy systems. This is still more conspicuous in the following section, dealing with intermediate phases. Unfortunately, only a few systems have yet

been examined with enough care to make wide generalisations possible. The ordered-disordered changes in solid solutions, on which the work of W. L. Bragg has thrown much light, are among the topics which are clearly treated. The last section discusses imperfections in crystal structure, including the various hypotheses of secondary or mosaic structures and of internal flaws, in their application to metals. Each section is provided with a bibliography, and the monograph, which is well produced, presents a wealth of information, and in addition is well fitted to provoke thought.

C. H. D.

Physikallisch-Chemisches Praktikum. By Dr. K. FAJANS and D. Jr. WURST (Zweite Auflage). (München, 1935.) Akademische Verlagsgesellschaft. M.B.H. Pp. xvi + 230. Price R.M. 10.80.

The original edition of this practical textbook of physical chemistry has become very popular, not only in Germany, but in other countries as well. It was made more available to English-speaking students by the translation in 1930 by B. Topley, and has since been translated into other languages. It was obviously written by men of considerable experience in teaching practical physical chemistry, and required very little alteration for this second edition. The most important alterations are the deletion of the chapter on "Viscosity," the addition of chapters on "The Determination of Partition Coefficients," on "Decomposition Potentials of Electrolytes," and on "Vapour Pressures." Not everyone will approve of the deletion and there is room for criticism in these new chapters. The inclusion of the mass law relations under the partition coefficient and the very approximate solutions of Nernst are now obsolete. This is the only reference to the mass law found in the book. There is no obvious reason for the inclusion of such subjects as "Decomposition Potentials" in a modern textbook. It would have been valuable to describe a method of determining the vapour pressures of liquids at temperatures above room temperatures rather than the simple case of ether below room temperature. One would like to have seen the apparatus used for spectrophotometry brought up to date. It is surprising to note that open mercury contacts are recommended in heater circuits for thermostats.

It is pleasant to see that the inconsistent thermodynamic nomenclature so common in German textbooks has been brought into line with modern practice in the new edition. The paragraph entitled "Difficulties and Sources of Error" at the end of each chapter is a welcome help to teachers of practical physical chemistry and an incentive to students for criticism of their experiments.

C. F. G.

Reports on Progress in Physics. Vol. II. The Physical Society. London 1936. Pp. iv + 371. Price, 21s.

The problem of how to keep pace with modern developments is one which besets every physicist. The Physical Society offers a solution of the problem in its annual Reports on Progress in Physics, the second volume of which, dealing with work up to the end of 1934 is now under review. The general scheme follows that of the first volume. In addition to reports

on the general parts of the subject (Heat, Light, Sound, Electrical Measurements, etc.) there are also more extensive articles on special subjects such as Geophysical Prospecting, Radio-exploration of the Upper Atmosphere, and Electron Tubes, together with a very useful paper on the Electronic Charge and accounts of recent work in Atomic Physics, Quantum Theory, X-rays and Spectroscopy.

It is manifestly impossible to discuss each section separately. The points of maximum interest will naturally depend on the predilection of the reader, but he may be assured that, wherever he reads, he will find authoritative accounts, with complete references, presented in most cases in a lucid manner. There are a few articles which can hardly be read profitably without a specialised knowledge of the subject, but they are outweighed by others which will evoke immediate interest. The general impression gained from a survey of the book is that the Physical Society has attempted to serve both the general reader and the specialist and, in the main, has succeeded in this object.

The amount of material in this volume is very considerable and for many it will serve as a textbook of modern work. The physical chemist will find much valuable information in the article on Atomic Physics and in parts of the reports on X-rays and Spectroscopy.

The printing and lay-out of the book are of the high standard always associated with the Cambridge University Press. There is a change of notation which might have been avoided in the article on Surface Tension, while the discussion on the determination of the electronic charge from X-ray measurements is repeated in the section on X-ray spectroscopy. These, however, are minor criticisms of a book which should be in the hands of all who would keep abreast of recent work.

R. H. H.

Dynamics of Rigid Bodies. By W. D. MACMILLAN. McGraw Hill, London, 1936. Pp. xiii and 478. Price, 36s. net.

Professor MacMillan's book is a welcome addition to the literature of dynamics. Without departing from the classical doctrine and tradition, he has shown that much work has been done, on strictly classical lines, since the days when Routh's great treatise dominated the subject. Certain mathematical methods, which are even now not so widely known as they might be, are necessary weapons of attack, and the author has provided admirably clear expositions of the relevant parts of vector algebra and of matrix theory.

The book begins at the beginning, but it presupposes some knowledge of the subject in those who would make the best use of it. The chapters which deal with the fundamentals of the subject follow lines in the main well-known, though the author, like every competent and thorough teacher, has his own point of view. The chapters on the differential equations of analytical dynamics, on the canonical equations of Hamilton, and on the difficult method of periodic solutions initiated by H. Poincaré, are models of their kind. Each chapter is illustrated by a large number of examples on which the reader may try his skill, and the book may be unreservedly recommended to the advanced student.

A. F.

The Revolution in Physics. By E. ZIMMER. Faber & Faber Ltd., London, 1936. Pp. xiv and 240. Price, 12s. 6d. net.

There is no end to the number of works which set out to tell the inquiring layman all about the change that has come over the innocent Victorian physics beloved of our parents—a change that has converted the physicist into a sometimes unwilling, sometimes enthusiastic, and always amateurish metaphysician. The present volume must be counted among the successes. The author discusses, easily and clearly, the nature of matter and of light according to classical physics, light quanta, the structure of the hydrogen atom and of the higher atoms, quantum mechanics and matter waves, science and philosophy. Mathematics is reduced to a few algebraical symbols and the translation reads admirably well. The price is low, and the book is produced in excellent fashion.

A. F.

The Quantum Theory of Radiation. By W. HEITLER. The Clarendon Press, Oxford, 1936. Pp. xi and 252. Price, 17s. 6d. net.

It was the failure of classical methods in the theory of radiation which led to the introduction of the quantum of action and the peaks in the resulting astonishing development occur in 1905, 1913, and 1925, the years that mark the hypothesis of light quanta, the application of quantum theory to the atom, and the beginnings of quantum mechanics.

Professor Heitler's volume is divided into five main sections which deal with the classical theory of radiation, the quantum theory of the field *in vacuo*, the interaction of radiation with matter, radiation processes concerned with positive electrons, and the penetrating power of high-energy radiation.

The name and personality of the distinguished author are sufficient guarantees of the full and scholarly treatment of the subject. The book is by no means easy reading, and the difficulties are not all mathematical, but it is quite indispensable to the advanced student of quantum mechanics.

A. F.

The Freedom of Man. By A. H. COMPTON. Humphrey Milford, London. Oxford Univ. Press, 1935. Pp. xi and 153. Price, 9s.

The last few years have seen an extraordinary growth of interest in philosophical questions, and the realms of the metaphysicians have been invaded by amateurs of very varied attainments—physicists, in particular, have found that studies of "fate, free-will, fore-knowledge absolute" have very important bearings on their own subject. Perhaps it would be better to reverse the statement and to say that, in the eyes of the physicist, his own subject has important contributions to make to that branch of philosophic thought which is concerned with the problem of determinism. That is, perhaps, not quite so certain as the physicist deems it to be, but it is all to the good that he should air his views. He imparts a welcome freshness to an old topic, even though he may make, with surprise and pleasure, discoveries in the realm of philosophy that are not much younger than Thales.

In the matter of determinism, the easy way out is that of Johnson—"Sir, we know we are free, and there's an end on't." True, we *know* we are free, but is that the end on't? What does freedom mean? Does it mean that our volitions are uncaused, or undetermined? If so, there is at once an end to the logical and practical reasons for rewards and punishments which, surely, may only be given on the assumption which, pragmatically, we know to be true, that they have very considerable effect on our future actions. I am free to choose, but that freedom by no means puts out of court the question—what determines my choice?

Professor Compton has chosen some aspects of this age-old topic for his Terry lectures. The heads of his addresses are—Freedom versus Law, What Determines our Actions, Intelligence in the World of Nature, Man's Place in God's World, and Death or Life Eternal. His addresses form a thoughtful and earnest contribution to a difficult problem. They appeal to a wide public and will be read with special pleasure by his many friends on both sides of the Atlantic.

A. F.

Advanced Laboratory Practice in Electricity and Magnetism. By E. M. TERRY and H. B. WAHLIN. McGraw Hill, London, 1936. Pp. xiv and 318. Price, 18s. net.

This, the third edition of Terry and Wahlin, does not require much introduction to English readers. The work discusses in comprehensive fashion, laboratory methods for the measurement of current, resistance, potential, power, capacitance and inductance. It deals further with photometry and pyrometry, oscillators and amplifiers, electron tubes and fundamental radio frequency measurements.

In the present edition, some of the experiments have been revised and two new experiments, on the determination of the electronic charge and on the determination of the thermionic work function of a metal have been added.

The chapter on electron tubes has been revised "in order to give the student some familiarity with the recent electron theory of metals, in particular as it applies to thermionic emission." In this work of revision, it would have been well if some of the later methods for the measurement of fundamental quantities had been introduced.

The book is not overloaded with detail but, although in one or two instances the descriptions incline to the sketchy side, in general they are quite adequate and the volume forms a very useful laboratory manual for advanced students in physics or in electrical engineering.

A. F.

SOME CHARACTERISTICS OF MERCURY—RARE GAS DISCHARGE TUBES.

BY H. W. MELVILLE.

Received 27th April, 1936.

In photochemistry, two ideals to be aimed at in the source of light are (a) constancy of output, (b) a sufficient degree of monochromatism. When dealing with sensitised reactions, the form of the exciting line or lines must also be known if the kinetics are to be studied in detail in order to derive the correct sequence of reactions comprising the total process. This is of particular importance in mercury sensitised reactions. If the exciting line is not narrow and unreversed, then the effect of added gases and of temperature on the shape of the absorption line of the mercury vapour in the reaction vessel may become so complicated that no real use of this method of initiating reactions can be made kinetically.

The usual type of mercury lamp having mercury-mercury, or mercury-tungsten electrodes with the cathode water cooled suffers from the disadvantages that it is unsteady, generates a considerable amount of heat, radiates lines besides the resonance lines at 2537 Å., 1860 Å. and emits, if the water cooling is not efficient, a partially reversed resonance line unless the additional complication of a magnet is employed to press the discharge against the walls of the lamp. Lamps with heated cathodes and tungsten anodes eliminate the majority of these disadvantages, although now it is necessary to control the temperature of the cathode accurately. This disadvantage is not, however, present in discharge lamps containing a mixture of rare gas and mercury vapour and running at some hundreds of volts A.C.

Commercial lamps of this type have been on the market for some time, consuming a small current—20 mA.—but no details regarding characteristics and outputs of bigger lamps working on this principle have been described so far as is known. The present paper gives details of the construction, operation and output of such a lamp capable of taking an input of 400 watts. The results also give a clue to the mechanism of the excitation of the mercury atoms in a discharge of this nature. Elsewhere its application to solving some problems in the exchange reactions of deuterium with hydrides will be described.

The shape and dimensions of the lamp are shown in Fig. 1. The end of the lamp is connected by a silica-soda glass joint to gas reservoirs, manometers and a pumping system. The electrodes are of iron sheet, as used in neon signs, one end being closed, welded to nickel wires and finally to 1 mm. tungsten wire which is sealed into the silica in the usual way by means of lead. The electrodes are water cooled in order to prevent the mercury pressure from rising too high. The lamp was excited from a 2000 v. transformer, the secondary current being controlled by a variable

resistance in the primary circuit. A few drops of liquid mercury were also present in the tube. Helium, neon and argon were used; the two latter gases were obtained from the British Oxygen Co. The neon contained a little helium and the argon was freed from the small amount of residual oxygen by passing over heated copper. The helium which contained some air was passed repeatedly through a charcoal tube cooled in liquid nitrogen. After each passage the charcoal was baked out at 300° in vacuo.

The absolute calibration of the lamp was carried out using as actinometric substances uranyl oxalate and monochloroacetic acid. The characteristics at different currents, voltages, etc., were determined by the less tedious method of measuring the mercury sensitised decomposition of ammonia since the lamp was designed expressly for use in sensitised reactions. The small amount of direct photodissociation was eliminated by interposing a 2 cm. layer of a 50 per cent. solution of acetic acid. The insulation tube for the decomposition of the ammonia was attached to a Pirani gauge and a mercury manometer. The procedure simply was to admit the ammonia to a pressure of about 100 mm., illuminate for the required time, condense out the ammonia with liquid air and measure the pressure of N_2 and H_2 by the Pirani gauge. This latter pressure was not

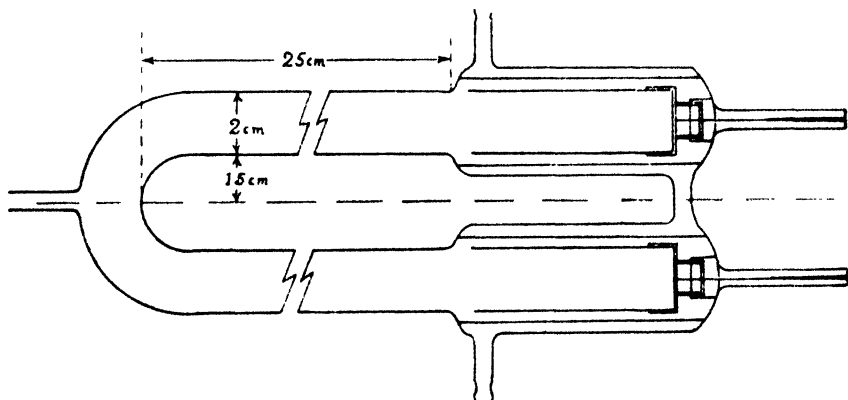


FIG. 1.

allowed to rise to more than 0.1 mm. so that the pressure of N_2 and H_2 produced is strictly proportional to the intensity of illumination. If the ammonia pressure is lower or if the decomposition is allowed to proceed further, the inhibitory effect of hydrogen tends to make the relationship between $p_{N_2} + p_{H_2}$ and time depart from linearity.¹

The variables to be considered are:—

Current, voltage, pressure, gas, temperature of lamp.

The effect of the temperature of the cooling water was not investigated as this remained at $12 \pm 1^{\circ} C$. When that part of the lamp exclusive of the electrode chambers is heated, practically no variation in output occurs up to as high a temperature as $600^{\circ} C$. Evidence for this statement will be given elsewhere. The three independent variables are the gas, its pressure and the current. The voltage is a function of all three, but fortunately it is not much dependent on the independent variables in the ranges used below.

Fig. 2 shows a set of experiments with argon in the lamp.

It will be seen, in the first place, that at a constant gas concentration the output increases with the current reaching a maximum and then

¹ Cf. Melville, *Proc. Roy. Soc., A*, 1935, 152, 327.

decreases. If, however, the pressure be maintained constant, the output becomes independent of current above 0.100 amp. It will also be observed that the output at constant current similarly increases with pressure and then decreases, as is seen from the lower curve, in which the results are plotted for a fixed current of 0.275 amp. Clearly there are optimum conditions for running the lamp. Besides the disadvantage of low output at low pressures, the electrodes begin to sputter at high current densities.

Experiments were also made to determine the time required for the lamp to reach a steady state, starting from cold. In one series after

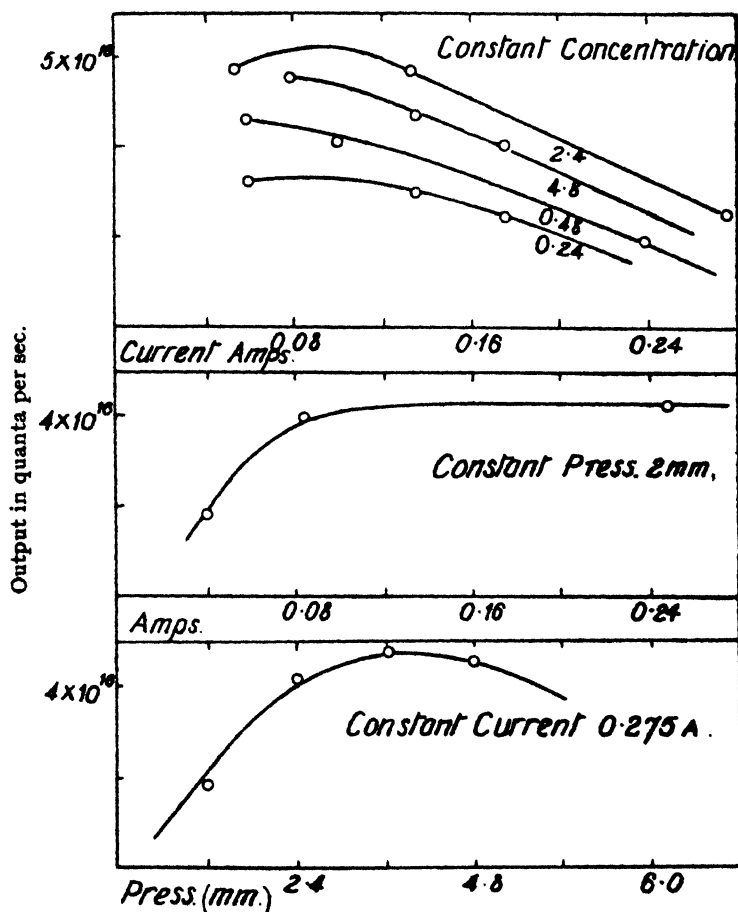


FIG. 2.—Argon. At 4.8 mm. the voltage varied from 850 to 1150; at 2.4 mm. from 850 to 1250; at 0.48 mm. from 700 to 1200; at 0.24 mm. from 550 to 1050.

10 min., 0.0925 mm. of N_2 and H_2 had been produced; within 30 min. the rate of production had risen to 0.15 mm./10 min. and remained stationary thereafter. Check experiments have been made at intervals during three months' use and no important variation in output (± 25 per cent.) was observed.

In a similar way the characteristics of the lamp were determined for neon. With this gas the lamp ran much cooler, more steadily, and over a wider range of pressure.

Again optimum conditions make their appearance, which are shown in Figs. 3a and 3b, where the output is plotted against current for different

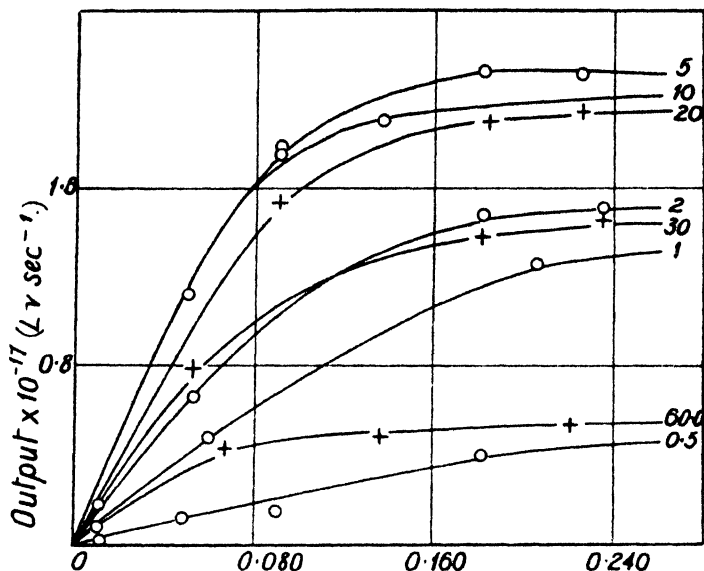


FIG. 3a.—Neon; effect of current. At 60 mm. the voltage across the lamp was 1000; at 30 mm. 700 to 850; at 20 mm. 500 to 550; at 10 mm. 400 to 470; at 5 mm. 400 to 570; at 2 mm. 430 to 580; at 1 mm. 440 to 530; at 0.5 mm. 500 to 680.

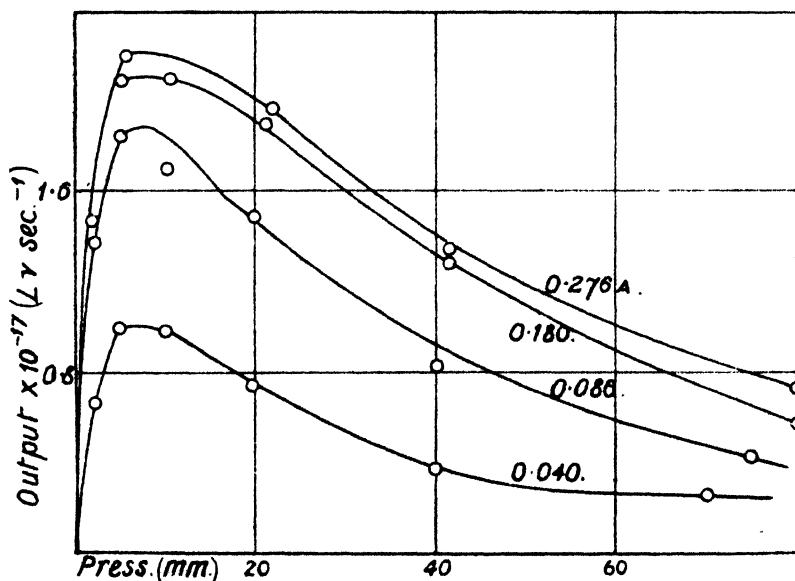


FIG. 3b.—Neon; effect of pressure.

operating pressures. When the output is plotted as function of the pressure at a constant current, Fig. 3b shows that a maximum occurs at about 6 mm. and is independent of the current. It is also apparent that no advantage

could be gained by increasing the current beyond 0.2 amp. A few results for helium are plotted in Fig. 4; the optimum pressure being 5 mm.

Hydrogen was also employed, but yielded a very small output. On pumping out the hydrogen and re-admitting neon the output was only 0.1 of that previously obtained and gradually decreased with time. Pumping out and refilling with neon improved the output. Apparently the hydrogen must have become adsorbed on the electrodes or on the sputtered iron and was only given up slowly on running the lamp. Helium proved to be more effective than neon in ridding the lamp of traces of hydrogen. Traces of hydrogen must, therefore, be rigorously excluded from the inert gas if a high output from the lamp is to be obtained.

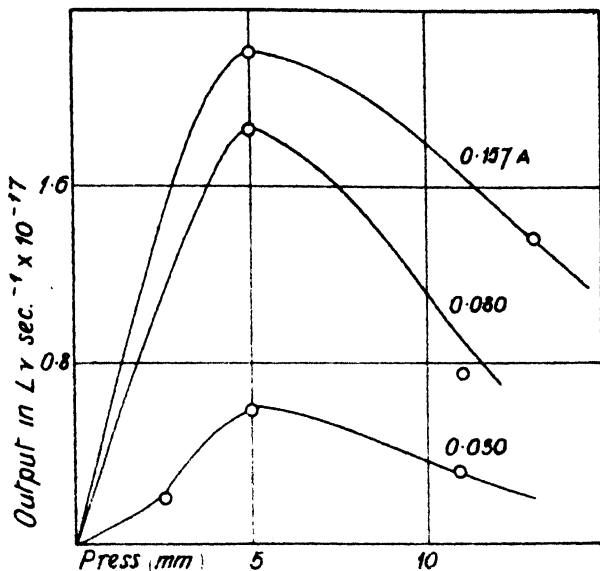


FIG. 4.—Helium.

The fraction of the total radiation of wavelengths less than 2300 was λ measured by observing the rate of the direct photo-chemical dissociation. The mercury vapour was frozen out of the ammonia by a trap cooled to -70°C . To get rid of the mercury vapour effectively the ammonia had to be passed through the trap very slowly, the total length being 20 cm., e.g., 15 c.c. at N.T.P. were passed through in 30 min. If the ammonia were passed through in a few seconds the partial pressure of the mercury was not reduced much below 0.0001 mm. For these experiments the acetic acid filter was removed. The rate of the direct decomposition was less than 10 per cent. of that of the sensitised.

Similar tests were made using the uranyl oxalate actinometer which is sensitive from 2000 to 4500 Å.² First a water filter was placed between lamp and reaction vessel and the rate of decomposition of oxalate measured. On substituting a 25 per cent. solution of acetic acid to cut out radiation of wavelength shorter than 2537 Å., the rate decreased to 70 per cent. of its previous value. Part of this reduction is certainly due to absorption of the 2537 line by acetic acid. On interposing a 3 cm. layer of CCl_4 which cuts off 2537³ the decomposition was reduced to 1 per cent. of its former value. Consequently at least 90 per cent. of the light emitted is at 2537 Å.

Absolute Output.

The absolute output of the lamp was measured by means of the uranyl oxalate actinometer based on the data of Forbes and co-workers. For

² Forbes and Heidt, *J. Amer. Chem. Soc.*, 1934, **56**, 2362.

³ Cf. Melville and Walls, *Trans. Faraday Soc.*, 1933, **29**, 1255.

example in one experiment the lamp was run under optimum conditions with neon as inert gas at 5 mm. pressure. The voltage was 370, the current 0.186 amp. and the input in watts 69. At a distance of 5.45 cm. an area $1.25 \times 8.55 = 10.7 \text{ cm.}^2$ received from one limb of the lamp 3.8×10^{17} quanta per second. Assuming even distribution of radiation from the lamp this corresponds to 1.33×10^{17} quanta per sec. per cm. length or 8×10^{18} total. This is equivalent to 8 watts and hence the luminous efficiency of the lamp works out at the relatively good figure of 11 per cent.

Mechanism of the Discharge.

The nature of the output-pressure curves at constant current give the clue to the probable mechanism of the excitation of the mercury atoms. The form of these curves is exactly similar to that obtained

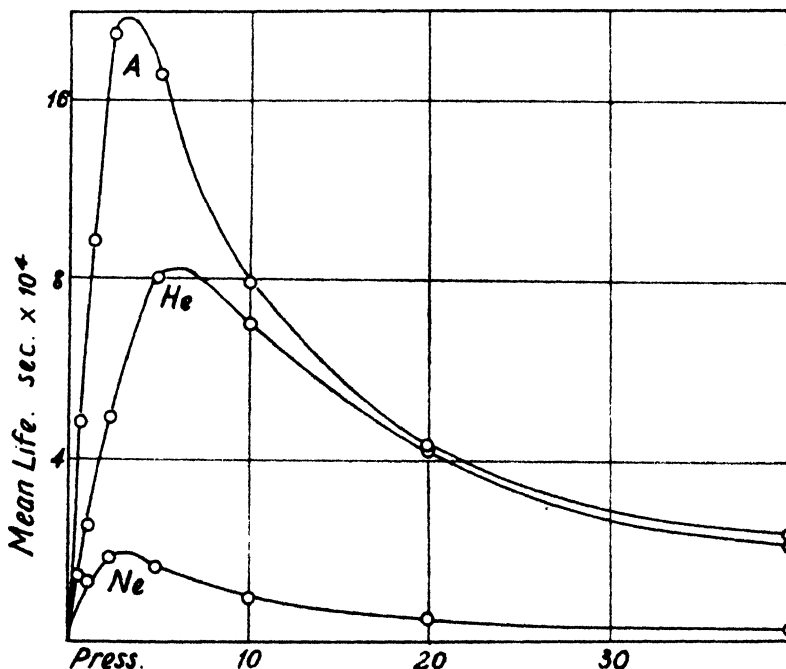


FIG. 5.

when the mean life (τ) of the metastable inert gas atom is plotted against pressure. From the results of Meissner,⁴ Eckstein,⁵ Ebbinghaus,⁶ and Anderson,⁷ it may be shown that metastable inert gas atoms are destroyed by diffusion to the walls of the discharge tube and by collisions in the gas phase with other inert gas atoms. The mean life may, therefore, be expressed by the equation

$$\tau^{-1} = B/p + Cp.$$

where B is proportional to the diffusion coefficient of metastable atoms through the gas and C is a constant containing factors such as the effective collision radius for the process which removes the metastable atom

⁴ *Ann. Physik*, IV, 1927, 84, 1009.

⁵ *Ibid.*, IV, 1928, 87, 1003.

⁶ *Ibid.*, V, 1930, 7, 267.

⁷ *Can. J. Res.*, 1930- , 2, 13; 1931, 4, 312.

to a higher (radiating) state. The value for B has been recalculated for a tube 2 cm. in diameter, and the data used to calculate the value of τ are given in the Table. τ is given in seconds if p is in mm.

The values of τ have been computed for the pressure range employed in operating the lamp and are plotted in Fig. 5. It can be seen at once that not only do the forms of the curves in Figs. 2, 3 and 4 exhibit similar shapes but that in addition

Temp. °K.	Gas.	B .	C .
300	Ne	2000	1100
300	A	160	120
80	A	15	170
300	He	1350	107

the maxima occur at about the same pressures. It may be concluded therefore that the output of the lamp is governed primarily by the concentration of metastable atoms. This hypothesis is supported too by comparing the inhibiting effects of hydrogen in the neon discharge. Eckstein⁵ found that 0.002 mm. hydrogen reduced τ for neon to half its value at a neon pressure of 2.12 mm. and it has been mentioned above that small traces of hydrogen reduce the output considerably.

It is difficult to draw any definite conclusions from these experiments regarding the nature of the collisions between the metastable atom and the mercury atom. The latter atom requires only 4.88 volts for excitation, whereas the smallest amount of energy the helium atom can communicate is 19.7 volts (2^3S_1), neon 16.5 volts ($3P_2$) and argon 11.5 volts ($3P_2$). In each case more than sufficient energy to ionise the mercury atom is available. The efficiency of the lamp is such, however, that the collisions between metastable inert gas atoms and mercury atoms must be very much greater than that between inert gas atoms involving the destruction of the metastable state. Since optimum conditions appear at about 5 mm. pressure, the mercury pressure being about 0.001 mm., the ratio of the collisions efficiencies would seem to be at least 5000 : 1.

Summary.

Some characteristics of mercury—rare gas discharge tubes have been measured in order to find optimum conditions for the running of a tube capable of dealing with an input of 400 watts and emitting the resonance line at 2537 Å. For an input of 70 watts it has been found possible to obtain an output of 10^{11} quanta per sec. At least 90 per cent. of the total radiation is at 2537 Å.

The optimum conditions occur at about the same values as those for the production of metastable inert gas atoms. Suggestions are made as to the mechanism of the collision processes taking place in the lamp on these bases.

The author is greatly indebted to Prof. E. K. Rideal for his constant encouragement during these experiments. He also thanks the Royal Commissioners for the Exhibition of 1851 for a Senior Studentship.

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THE MECHANISM OF THE FORMATION OF FOGS BY ULTRASONIC WAVES.

BY KARL SÖLLNER.

Received 20th July, 1936.

This paper deals with the mechanism of the formation of fogs, *i.e.* with the "atomisation" of non-metallic liquids by ultrasonics.

I.

This phenomenon, first described by W. R. Wood and A. L. Loomis,¹ has not been investigated thoroughly, although the opposite phenomenon, the coagulation of smokes and fogs, has been studied.²

Wood and Loomis describe the formation of fogs by ultrasonics about as follows. In the case of such fairly volatile liquids as benzene, toluene, water, etc., it is best shown by dipping a beaker containing a little of one of these liquids in the oil over the vibrating quartz. The beaker fills rapidly with a white cloud—a fog of benzene. This fog is in a continuous tumultuous motion.

To produce fogs of less volatile liquids, *e.g.*, of transformer oil—as used for the oil bath—another arrangement must be used. A test-tube of about 2.5 cm. diameter is drawn out in the middle to a diameter of about 7 mm. The constriction must be rather thin-walled to allow large amplitudes of the transverse vibrations set up in the glass, otherwise the effect is weak, or unobservable. When this "collector" is dipped into the oil bath the oscillations of the glass are very vigorous at the constriction. If a little oil is now applied to the outside of the tube above the constriction, it "spreads over the surface and is thrown out in jets of spray resembling smoke and a dense cloud gathers about the tube." Close inspection shows that the oil on the collector gathers in more or less regular rings which form dots here and there, and the jets of spray are shot out from these dots.³

II.

Having regard to the strong heat effects, usually found when irradiating with ultrasonics (and specially mentioned in the case of the collector by Wood and Loomis), one is inclined to consider the cause of the formation of fogs as a temporary evaporation followed by a rapid condensation. But this explanation can easily be discarded by using solutions containing a non-volatile compound, conveniently a dyestuff. Both in the beaker as with the collector—and in the latter case still more strikingly—the formation of coloured fogs is seen readily, hardly any residue of the non-volatile substance being left, after the whole liquid has

¹ W. R. Wood and A. L. Loomis, *Phil. Mag.*, 1927, 4, (7), 417.

² Cf., *e.g.*, O. Brandt and E. Hiedemann, *Trans. Faraday Soc.*, 1936, 32, 1101; *Kolloid Z.*, 1936, 75, 129; E. N. da. C. Andrade, *Trans. Faraday Soc.*, 1936, 32, 1111.

³ As to photographs of this phenomenon, see the paper of Wood and Loomis, *loc. cit.*¹

been dispersed into the air. Thus, temporary evaporation is excluded as the cause of formation of fogs.

Another, at first rather attractive, possibility may be seen in the fact that during strong local irradiation all liquids form mounds or fountains, which throw drops of the liquid into the air. Such a fountain is always seen in the oil bath at higher energies.³ But the two phenomena, the oil fountain dispersing drops and the formation of a true fog, are quite different and independent of each other. They may be separated easily.

With substances of high viscosity (*e.g.*, paraffin-oil) a fountain, dispersing drops, is always found with medium and high energies, but the formation of a fog is only to be seen at such very high energies as endanger the quartz oscillator. With less viscous and more volatile substances (*e.g.*, ether, alcohol, benzene, etc.) contained in a beaker or test-tube fogs are easily formed at room temperature, or with less volatile and more viscous liquids at higher temperatures, using energy densities such as 20, 30, 40 mA. (according to the substance), which produce no oil fountain in these liquids; only the very small droplets form the fog. With increasing energy a point is reached, where, in addition to increased fog formation, a distinct fountain of liquid may be seen and with slightly higher energy, drops of considerable size are torn away and thrown into the air.

The drops dispersed by the oil fountain have with all substances diameters between several tenth and several millimetres,³ whereas the fog droplets are so small that the fogs are stable for several seconds at least, often for several minutes. (Ultrasonics do not, then, at present provide a satisfactory method for preparing fogs, since other methods yield much smaller fog droplets, *i.e.*, much more stable fogs.)

The same applies to the collector. Here, due to the concentration of the energy, such vehement oscillations are set up in the constriction that substances like paraffin-oil may easily be dispersed, when the quartz vibrates only with normal energy.

At first sight one is inclined to the view that the fog droplets are thrown out from the jets, as described by Wood and Loomis.³ But one wonders, how such small droplets can obtain sufficient energies to travel so vigorously through the air, whereas bigger drops, which occasionally (when much liquid is present on the collector) are thrown out, do not possess a high velocity and fall into the oil bath quite close to the collector. This is explained by the observation that strong air currents are set up in the neighbourhood of the vibrating collector;⁴ these air currents are strong enough to push the flame of a micro-Bunsen-burner horizontally sideways, when brought close to the collector.

Obviously these air currents are responsible for the movement of the fog droplets and the whole appearance of the phenomenon. But they do not explain the primary formation of the fog droplets.

We must therefore discard the explanation that the fog droplets are simply thrown out from the surface of the irradiated liquid, as are the big drops from the oil fountain or the collector.

We emphasise that the collector shows no new features, as compared with the simple oil fountain, but provides a method of concentrating the energy for studying phenomena, which otherwise could not be obtained

⁴ That an ultrasonic oscillator may produce air currents is a well-known fact, *cf.*, *e.g.*, A. Meissner, *Physik. Z.*, 1927, 28, 621; *Naturwiss.*, 1929, 17, 25.

without endangering the quartz. It produces quite generally strong mechanical actions; *e.g.*, it is very efficient in emulsifying, if drops of two immiscible liquids are put on the constriction.

III.

An indication as to the true mechanism of the fog formation may be seen in the fact that the surface always becomes rippled as if it were being hit from above, just before fog formation sets in.

Previous experiments ^{5, 6} have shown that surfaces are always a locus of strong mechanical action—due to cavitation as defined earlier; ⁵ it therefore seems reasonable to assume that one is here also dealing with cavitation. To prove this two methods have always been employed: the mechanical effects disappear both when cavitation is rendered ineffective (due to lack of outside pressure), when experimenting in vacuo, and when a sufficiently high external gas pressure is applied (the liquid not being saturated with the gas) thus rendering the disruption of the liquid impossible.

Obviously the latter method cannot be applied in the present case, as the surface, where the fog is formed, is in contact with the gas, and saturation, in the extremely narrow zone with which we are concerned, occurs much too rapidly, to allow conclusive experiments. ⁷

When experimenting in vacuo things seemed at first sight to be less simple than usual, but the final cause of the difficulties found, also explains a phenomenon of minor importance in the formation of emulsions, which has so far been inexplicable. (See below.)

Liquids with a low vapour pressure (*e.g.*, as tetraline, decaline, low viscosity paraffin-oil, etc.), behaved normally and yielded fogs at atmospheric pressure, but not when carefully degassed and sealed in vacuo in test-tubes, even with such strong irradiation that considerable fountains were formed in the liquids and large drops abundantly thrown out from the surface. The surface also lacked the characteristic rippled appearance, always associated with fog formation.

The more volatile substances, *e.g.*, ether, benzene, toluene, water, etc., however, somewhat unexpectedly yielded fogs in vacuo. This fog formation becomes stronger and stronger when the samples get warm after prolonged irradiation, and when heated intentionally to 40° or 50° C. before irradiation they yield very dense fogs.

The less volatile substances also showed fog formation when heated considerably prior to irradiation, or when heated by very prolonged irradiation. Correspondingly fog formation is not observed when the vacuum samples of ether, benzene, toluene, etc., are cooled down considerably prior to irradiation. The temperature where fog formation stops, depends upon the nature of the liquid (and to some extent upon the energy applied). Benzene and water, *e.g.*, do not yield fogs, when cooled to 4° and 0° C. respectively; ether must be considerably colder to prevent fog formation.

⁵ *E.g.*, C. Bondy and K. Söllner, *Trans. Faraday Soc.*, 1935, **31**, 835.

⁶ K. Söllner and C. Bondy, *Trans. Faraday Soc.*, 1936, **32**, 616; H. Freundlich and K. Söllner, *Trans. Faraday Soc.*, 1936, **32**, 966.

⁷ For this reason all experiments with pressure ^{5, 6} have so far been performed with high columns of liquid or gel, thus preventing saturation at the critical spot. The meniscus, being in contact with the compressed gas, was always found to be a locus of cavitation. Just as the formation of fogs cannot be prevented by gas pressure, so emulsification cannot be prevented if just a drop of a second liquid floats on the top of another and gas pressure is applied.

Thus, we see that the difference between the more and the less volatile substances is only due to the temperature limit, below which the formation of fog in vacuo (more correctly its formation in the absence of a foreign gas), does not occur on irradiation.

The effect of lowering the temperature is not found in presence of a foreign gas, the influence of which may be seen even at such fairly low pressures as 20 or 50 mm. Hg, depending upon the substances under investigation, the temperature (so far it affects viscosity) and the energy applied.

The simplest explanation of these facts is to assume that cavitation may be rendered effective not only by a foreign gas but also by a sufficiently high vapour pressure of the irradiated liquid itself, acting in the same way as the "gas pressure" mentioned so often in previous papers. This theory of fog formation also agrees with the fact that the liquid/air interface has always been found to be the locus of the most intense cavitation effect.^{5, 6}

The effect of the vapour pressure of the irradiated substances was demonstrated by the following experiment: a sealed test-tube containing, e.g., a few c.c., each of carefully degassed benzene and water, yields no emulsion on irradiation, even at very high energies.⁵ But on heating the whole test-tube, e.g., to 50° or 80° C., emulsification sets in at once on irradiation (even with medium energy) and soon both layers of liquids are turbid, first the benzene and shortly afterwards also the aqueous phase.⁸ It also becomes clear now why after very prolonged "irradiation in vacuo" a slight emulsification is often noticed.

One may therefore safely conclude that the formation of fogs is due to the same mechanism as all other disruptive and destructive effects in non-metallic systems, i.e. to "cavitation."⁵ In these systems a gas pressure is always necessary to render cavitation effective; usually it is due to the presence of a foreign gas but it may also be due to the vapour pressure of the liquids themselves, provided it is not too low. Though cavitation is less vigorous it is still sufficient to produce effects. The close parallelism between emulsification and fog formation is obvious.⁹

⁵ Emulsification—preferably in the aqueous phase—at increased temperature "in vacuo" is not nearly so strong as at room temperature under atmospheric (equilibrium) pressure. But emulsification under equilibrium pressure at increased temperature is also less strong than at room temperature. This may be due in part to the lower viscosity, and also to the reduced vigour of the collapse of the cavities. Emulsification "in vacuo" is increased if the whole test-tube containing the liquids is heated so that the pressure over the liquid is not reduced by condensation on the glass.

⁹ Vehement ultrasonic vibrations may also produce fogs of liquid metals. When a drop of mercury or molten Wood's metal is allowed to run down inside a collector tube, as described before, a cloud of dispersed metal is formed inside the collector at high energies. The mechanism of this dispersion process seems to be quite different from that holding for non-metallic substances, in analogy with the difference of the two mechanisms of the formation of emulsions in water/oil and water/metal systems respectively. (Cf. C. Bondy and K. Söllner, *Trans. Faraday Soc.*, 1931, 31, 843.) The formation of metal fogs is not due to cavitation, as it occurs also *in vacuo*. Probably the liquid metal is thrown from one side to the other of the constriction, the continuous impacts breaking down the drops, the finest ones being finally driven away by the air currents thus forming a visible cloud.

IV.

The insight into the mechanism of fog formation by ultrasonics may be of some importance, when trying to develop this method (using liquid energy transmitters) on a technical scale or for calling forth still bigger effects.

We can now link up the breaking of quartz oscillators as it happened twice to the author at the beginning of his investigation in a reasonable manner with the formation of a strong fog in the oil bath. The latter appears when cavitation is strong in the oil bath. But when this happens the limiting value of the energy transmission is reached,¹⁰ the excess energy can no longer be transmitted, the quartz oscillators vibrating more and more vigorously; finally it breaks. Quartz oscillators vibrating in air (where the energy transmission is very poor) must not be excited with more than a few watts, otherwise they crack, but in an oil bath they stand the application of several hundred watts for practically unlimited time.

Hence, to keep the quartz intact energy densities close to those where fog is formed in the oil bath are to be avoided; and a substance with a low vapour pressure at room temperature, such as paraffin-oil, is suitable as oil bath, in agreement with our experience; it ought not, however, to have too high a viscosity, as the damping of the vibrations increases with higher viscosities.

From a purely theoretical point of view it would therefore be advisable to use as oil bath a carefully degassed, not too viscous liquid with a high boiling-point under a considerably hydrostatic pressure contained in a vessel closed all round—a device not easily realised. Furthermore the ideal liquid ought to have a high specific gravity and a great sound velocity, to increase the energy transmission from one phase to the other as much as possible.¹¹

My heartiest thanks are due to Professor H. Freundlich for his continuous interest in this work and his helpful criticism. I am also greatly indebted to Professor F. G. Donnan, F.R.S., for his generous hospitality.

Summary.

1. The formation of fogs of non-metallic liquids by ultrasonic waves is due to the same mechanism as all the other disruptive and destructive effects of ultrasonics, namely to cavitation, or more correctly to the vehement collapse of cavities.

2. This collapse may be brought about by an external gas pressure or in the absence of a foreign gas by the vapour pressure of the irradiated liquid itself, provided that this vapour pressure is not too small; for this reason fog formation stops at low temperatures in absence of a foreign gas.

3. The fact that the vapour pressure of irradiated liquids—in absence of a foreign gas—can effect the collapse of cavities explains also the fact that at higher temperatures the process of emulsification proceeds also “in vacuo,” i.e., in absence of a foreign gas.

4. The importance of fog formation in the oil bath for the technique of ultrasonics and for its further development is shortly discussed.

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¹⁰ Cf. preferably the papers of R. W. Boyle and co-workers, e.g. Boyle, *Science Progress*, 1928, **23**, 75; *Trans. Roy. Soc. Can.*, 1922, **16**, 157; Boyle and Taylor, *Physic. Rev.*, 1926, **27**, 518; Boyle and Froman, *Report Can. Research Council*, June, 1927.

¹¹ Cf. e.g., the comprehensive account on energy transmission by E. Hiedemann in *Ergeb. exakt. Naturwiss.*, 1935, **14**, 227 ff.

EXPERIMENTS TO DEMONSTRATE CAVITATION CAUSED BY ULTRASONIC WAVES.

BY KARL SÖLLNER.

Received 26th July, 1936.

In some previous papers it has been shown that all the disruptive and destructive phenomena caused by strong ultrasonic waves in non-metallic systems must be attributed to "cavitation."¹

If a liquid is by some means stretched unduly it disrupts, cavities are formed, and when now an external force, e.g., hydrostatic pressure acts upon these cavities, they collapse vehemently—according to Lord Rayleigh the total volume energy of the cavities is thus concentrated in a very small spot. This whole process, the formation and the vehement collapse of cavities, was called "cavitation."²

That cavitation occurs when irradiating a liquid system with ultrasonics of high energy was deduced from theoretical reasons and from many cases of (experimental) analogy.

Cavitation was actually observed some sixty years ago by Kundt and Lehmann,³ when experimenting with sound waves, as ensues from their statement: "While the whole system was vibrating vigorously we several times noticed that the water close to the end of the vibrating rod turned turbid. Since it was entirely free from air, these small bubbles causing the turbidity could only be due to the disruption of the water (*Zerreißen in kleine Partien*) under the influence of these intense vibrations." Cavitation in a streaming liquid also was demonstrated by Osborne Reynolds.⁴

So far, however, cavitation has not been actually seen with ultrasonics, because we were mainly interested in two-phase systems (e.g., when studying emulsification) when experimenting with ultrasonics of high energy. The phenomenon was soon observed visually when investigating the formation of fogs,⁵ where only a single phase is irradiated and no opacity hinders the observation as is the case when emulsions are formed.

The experiments must be carried out with degassed liquids to avoid the formation of gas bubbles when irradiating. To ensure this the liquids, contained in big test-tubes, are kept in the vacuum of a filter pump and the tube knocked with a piece of wood for a considerable time until, when the gas is driven out sufficiently, the glass tube starts vibrating and emits a musical tone. (The knocking has qualitatively the same effect, as the

¹ C. Bondy and K. Söllner, *Trans. Faraday Soc.*, 1936, **31**, 835; H. Freundlich and K. Söllner, *ibid.*, 1936, **32**, 966; K. Söllner, see preceding paper.

² "Cavitation" must not be confounded with the degassing action of sound waves, which is sometimes called cavitation in the literature.

³ A. Kundt and O. Lehmann, *Ann. Physik* (Pogg.), 1874, **153**, 1.

⁴ See historical introduction, C. Bondy and K. Söllner, *Trans. Faraday Soc.*, 1936, **31**, at page 836.

⁵ See preceding paper.

sound waves—the liquid is stretched; for the same reason, superheated liquids start boiling on tapping.)

The phenomenon described below is best seen with liquids of not too high a boiling-point, *e.g.*, benzene and toluene or, preferably, water at a slightly higher temperature; nitrobenzene, *e.g.*, has to be heated (40–50° C.) to give well-visible results.

Not too short columns, 10–40 cm. high, of liquid are filled into U-tubes of moderate diameter or into long test-tubes. Before beginning the experiment it is advisable to irradiate for several minutes with high energy (100–130 mA.) to drive out the residue of gas invariably present.

When the liquid in these tubes is observed now (in transmitted light) whilst the energy applied is gradually increased, first a formation of fog is seen at the surface; with somewhat higher energy (best to be seen in narrow tubes) a few bubbles are formed at more or less regular half-wave distance from the surface, and the hissing noise, always to be heard when cavities collapse, increases. On stopping the irradiation suddenly the few bubbles rise to the surface. This hissing noise is a very helpful practical indicator as to the efficiency of irradiation. Although its loudness differs for different systems at the same intensity of irradiation since the readiness to cavitate differs with different systems—it is characteristic for each system. (So when trying to get reproducible results in a serial investigation, the test-tubes containing the different specimens are always dipped into the oil fountain in such a position that the same (maximum) noise is heard.)

With still higher energy the noise increases still more and slightly opaque and glittering zones are formed. In the narrow tubes they often have the form of a narrow funnel, which seems to be fixed to the glass wall. Obviously cavitation starts here at a spot on the wall where the disruption occurs more easily, due to some impurity, the adhesion being smaller than the cohesion of the liquid.

In these opaque zones a strong upward movement is to be seen. In the wider tubes the slightly glittering zones of opacity often move vigorously upwards and vanish suddenly. Hardly any, very small gas bubbles and in the best experiments none at all seen emerging from these zones of opacity. As soon as cavitation starts vigorous movement sets up in the interior of the liquid, as well as vigorous movement of any suspended impurities. So when experimenting with a diluted suspension in a narrow tube the zones of accumulation always formed in the middle of the tube are destroyed at once.

The whole phenomenon—although the opacity is considerably smaller—has the same appearance as the phenomenon of Osborne Reynolds mentioned above; one has the impression that the water is disrupted internally. One is obviously here dealing with the same phenomenon as described by Kundt and Lehmann⁶ for lower sound frequencies, *i.e.*, one is observing true cavitation as defined above.

As usual⁶ cavitation is rendered impossible, when a sufficiently high gas pressure is applied (the liquid being degassed), the zones of opacity are not formed any longer. In vacuo also the phenomenon ceases, bubbling and boiling of the liquid setting in.

Summary.

Cavitation by ultrasonic waves may be made directly visible, if long columns of degassed liquids are irradiated with high energy. Slightly glittering zones of slight opacity, which disappear without producing gas bubbles, are formed in the liquid when it disrupts, due to the stretching by the ultrasonic waves.

⁶ *Loc. cit.*¹ and K. Söllner and C. Bondy, *Trans. Faraday Soc.*, 1936, **32**, 616.

I am very thankful to Professor H. Freundlich for his continuous interest in this work, and am also greatly indebted to Professor F. G. Donnan, F.R.S., for his hospitality.

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THE DIFFRACTION OF ELECTRONS BY MOLYBDENITE.

BY G. I. FINCH AND H. WILMAN.

Received 23rd July, 1936.

1. Introduction.

Impurities in one form or another are now well recognised as a source of "extra" rings in electron diffraction patterns.^{1, 2, 3, 4, 5, 6} We have, however, recently obtained "extra" diffractions from graphite under conditions which were shown to exclude impurities as a possible origin, and have found further that such "extra" diffractions were in some way connected with the extreme thinness of the graphite flakes examined.^{7, 8} It was concluded that these "extra" diffractions obtained from graphite were due to the fact that in thin flakes the graphite lattice, though virtually unbounded in the cleavage plane directions, is limited in the remaining dimension by the thinness of the crystal, thus giving rise to diffractions of fractional l index, and also to diffractions of integral l values, but otherwise forbidden by considerations of structure factor as applying to the unlimited lattice. The close agreement obtained between the observed and calculated spacings corresponding to the "extra" diffractions of graphite supports this view.

In a previous communication² we described the effect of rotation of a thin mica crystal about an axis perpendicular to the beam. It was then observed that the normal hexagon pattern appeared to elongate continuously with rotation of the specimen. The phenomenon was not recorded photographically, however, which was unfortunate, because the mica crystal was very thin, yet appeared to be exceptionally free from distortion and had, furthermore, been so successfully mounted in the axis of the specimen carrier stem that the crystal remained in the beam during rotation through a relatively large angle. Darbyshire and Cooper,⁹ using bent mica crystals, sought for but failed to observe the phenomenon, which should give rise to streaks in the pattern. This

¹ Finch, *Proc. Phys. Soc.*, 1934, **47**, 123.

² Finch, Quarrell and Wilman, *Trans. Faraday Soc.*, 1935, **31**, 1050.

³ Mark, Motz and Trillat, *Naturwiss.*, 1935, **20**, 319.

⁴ Finch and Quarrell, *Nature*, 1935, **136**, 720.

⁵ Preston and Bircumshaw, *Phil. Mag.*, 1936, **21**, 713.

⁶ Aylmer, Finch and Fordham, *Trans. Faraday Soc.*, 1936, **32**, 864.

⁷ Finch and Wilman, *Nature*, 1936, **137**, 271.

⁸ Finch and Wilman, *Proc. Roy. Soc., A*, 1936, **155**, 345.

⁹ Darbyshire and Cooper, *Proc. Roy. Soc., A*, 1935, **152**, 104.

might, however, have been due to the considerable thickness of their specimen; thus Darbyshire and Cooper's mica pattern shows strong Laue zone spot intensification, and their mica crystal must therefore have been much thicker than ours. However this may be, we have since then recorded ⁸ streaks passing through diffraction spots in certain transmission patterns from graphite crystals which were so thin as to be practically transparent and colourless.

These new phenomena of "extra" diffractions and streaks obtained with very thin crystals are of such fundamental importance in their bearing upon the mechanism of electron diffraction and the interpretation of the pattern that we have turned our attention to the diffraction of electrons by other layer lattices with the object of submitting our previously advanced views ⁸ to further experimental test. In what follows an account is given of the diffraction of electrons by thin flakes of molybdenite, a mineral of relatively simple lattice structure. Patterns from mica were also obtained; though unsuitable for quantitative discussion, owing to the complexity of the structure, they served to illustrate more generally the effect of flake thickness upon the pattern.

2. Experimental.

Camera No. 2 (Cambridge) was used. The effective camera length and beam accelerating potential were about 50 or 28 cms. and 50 KV. respec-

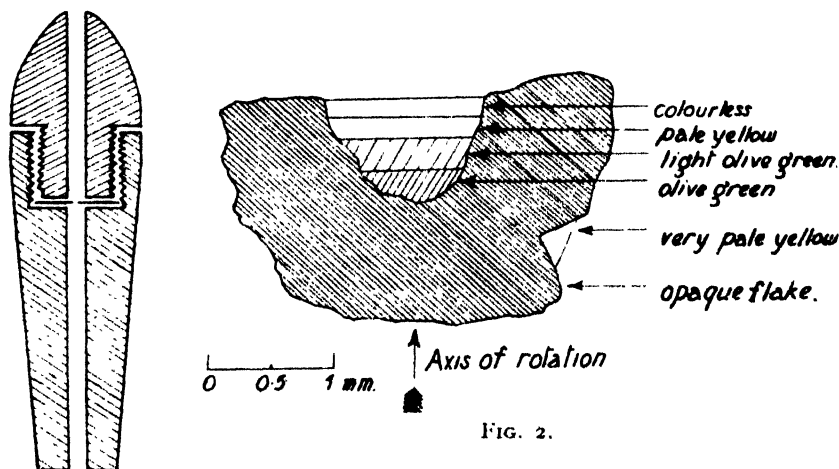


FIG. 2.

FIG. 1.—Anode Diaphragm.

tively. A new type of anode diaphragm was employed in order to obtain the high degree of resolution aimed at as necessary for significant measurement of the diffraction patterns. A 32 S.W.G. nickel or platinum disc was perforated by driving the point of a fine needle, embedded in a cork as guide, through the disc resting on a thick sheet of aluminium. The disc was then firmly clamped in the brass diaphragm holder, Fig. 1.

Two excellent specimens of gangue-free molybdenite were selected for us by Dr. Jones from the Royal School of Mines collection. Single crystals, suitable for transmission, were prepared in the manner previously described ⁸; they were so thin as to be translucent and varied, according to thickness, between almost colourless and dark reddish-brown.

3. The Structure of Molybdenite.

Molybdenite has a hexagonal layer structure.^{10, 11, 12} The co-ordinates of the molybdenum and sulphur atoms in molybdenite are $(1/3, 2/3, 1/4)$; $(2/3, 1/3, 3/4)$; and $(1/3, 2/3, u)$; $(2/3, 1/3, u + 1/2)$; $(2/3, 1/3, -u)$; $(1/3, 2/3, 1/2 - u)$ respectively, where $u = 0.62$. Hence the structure may be regarded as built up of layers, each consisting of a plane hexagonal network of molybdenum atoms sandwiched in between two similar networks of sulphur atoms. The projections of the molybdenum atoms pass through the centres of interstices in the sulphur sheets, the atoms of which are directly superimposed. Successive layers are so ordered that the sulphur atoms of one layer lie on projections passing through the centres of the interstices of the sulphur sheets in the neighbouring layers. Wyckoff¹³ gives the dimensions of the unit cell as $a = 3.15$ Å and $c = 12.30$ Å.

Yamaguti¹⁴ and Aminoff and Broomé¹⁵ have obtained electron diffraction patterns of the cross-grating type from molybdenite but observed only normal spectra.

4. The Results from Molybdenite.

Molybdenite crystals of in all eight different orders of thickness were examined. The corresponding colours in transmitted white light and the types of diffraction pattern yielded are given in Table I.

TABLE I.—PROPERTIES OF MOLYBDENITE TRANSMISSION CRYSTALS.

Colour.	Approximate Radius of Zero Order Zone ($L = 28$ cms. and $V = 50$ KV.) in cm.	Other Features.	Estimated Order of Thickness in Å.
Almost colourless.	Indefinite, as zero and first order zones coalesced.	Brilliant cross-grating patterns, exceptionally free from background.	≤ 40
Very pale yellow.			< 40
Pale yellow.			< 40
Light olive-green.	1.5	First order Laue zone very faintly defined.	≈ 40
Olive-green.	1.0	Faint first order Laue zone. Traces of Kikuchi lines.	≈ 100
Dark olive-green (brownish).	0.7	Narrow first order Laue zone; a few faint Kikuchi lines.	> 100
Light brown.	—	Background becoming prominent; clear Kikuchi lines.	≈ 100
Brown.	—		
Red.	—	Strong background.	Probably > 1000

The thickness of the flakes of light olive-green colour was estimated from the extent of the Laue zones of bright spots in the diffraction pattern

¹⁰ Dickinson and Pauling, *J. Am. Chem. Soc.*, 1923, **45**, 1466.

¹¹ Hassel, *Z. Krist.*, 1925, **61**, 92.

¹² Natta, *Gazz. chim. ital.*, 1926, **56**, 651.

¹³ Wyckoff, *The Structure of Crystals*, 1931, 2nd ed., New York.

¹⁴ Yamaguti, *Proc. Phys. Math. Soc. Japan*, 1932, **14**, 57.

¹⁵ Aminoff and Broomé, *Z. Krist.*, 1935, **91**, 77.

as being of the order of three unit cells,¹⁶ though in view of the double scattering which almost certainly occurs¹⁶ this is probably somewhat of an underestimate. The pale yellow, very pale yellow and almost colourless flakes were evidently successively still thinner, as was shown also by the progressive increase in extent and brilliancy of the corresponding cross-grating patterns and the extreme fragility of such specimens.

(a) **Multi-spot Patterns from Thin Crystals.**—Thin, pale yellow crystals adhering by only one edge to the thicker material gave patterns, when stationary, of the type shown in Fig. 3. Even under a low magnification, it was evident in the microscope that such crystals were much crinkled and torn and, indeed, distorted to such an extent that practically all normal diffractions might be expected to occur, no matter how the crystals were set up in the beam. The analyses of Fig. 3 and of two other patterns of similar type obtained from different specimens are summarised in Table II.

TABLE II.—ANALYSIS OF PATTERNS FROM CRINKLED MOLYBDENITE FLAKES.

d in Å. (Electron Diffraction Results Reduced to $(d_{110})=1.575$ Å.)	Number of Diffractions Measured.	Indices of Normal Diffractions in Agreement with X-rays.	Possible Indices of Anomalous Diffractions.	d in Å. Corresponding to Indices Assigned to the Anomalous Diffractions.
9.50	1	These anomalous diffractions lying within the 100 ring are unexplained. They are not due to grease, with the spacings of which they have nothing in common, but appear to be associated in some way with strong distortion of thin MoS_2 crystals.		
9.38	4			
8.18	1			
7.37	2			
6.31	3			
5.90	2			
5.85	5			
5.68	2			
5.40	2			
5.28	2			
5.19	2			
5.02	1			
4.802	4			
4.769	2			
4.495	4			
4.469	4			
4.434	5			
4.282	9			
3.812	8			
3.728	6			
3.700	6			
3.637	5			
3.587	2			
3.560	2			
3.534	2			
3.458	2			
3.387	3			
3.327	2			
3.245	4			
3.228	3			
3.193	8			
3.174	5			
3.142	3			
3.081	3			
3.050	1			
2.966	3			
2.944	2			
2.845	3			
2.796	2			
2.766	3			

¹⁶ Finch and Sun, *Trans. Faraday Soc.*, 1936, **32**, 852.

TABLE II.—*Continued.*

<i>d</i> in Å. (Electron Diffraction Results Reduced to (<i>d</i> ₍₁₁₀₎ = 1.575 Å.)	Number of Diffractions Measured.	Indices of Normal Diffractions in Agree- ment with X-rays.	Possible Indices of Anomalous Diffractions.	<i>d</i> in Å. Corresponding to Indices Assigned to the Anomalous Diffractions.
2.729	10	100		
2.695	1		10 ₁ ² ; 10 ₂ ² ; 10 ₃ ²	2.690; 2.702; 2.694
2.663	11	101		
2.635	2		10 ₁ ³ ; 10 ₂ ³ ; 10 ₃ ³	2.629; 2.636; 2.641
2.539	2		10 ₁ ⁴ ; 10 ₂ ⁴	2.544; 2.534
2.496	13	102		
2.440	2		10 ₁ ⁵	2.440
2.425	1		10 ₁ ⁶	2.422
2.393	3		10 ₁ ⁷	2.387
2.375	1		10 ₁ ⁸ ; 10 ₂ ⁸	2.363; 2.370
2.352	2		10 ₁ ⁹ ; 10 ₂ ⁹	2.358; 2.356
2.340	2		10 ₁ ¹⁰	2.337
2.320	4		10 ₁ ¹¹ ; 10 ₂ ¹¹	2.328; 2.317
2.308	2		10 ₁ ¹²	2.309
2.295	9		10 ₁ ¹³	2.303
2.285	1		10 ₂ ¹³	2.286
2.271	12	103		
2.251	3		?	
2.243	9		10 ₁ ¹⁴	2.243
2.223	6		10 ₁ ¹⁵	2.224
2.203	5		10 ₁ ¹⁶ ; 10 ₂ ¹⁶ ; 10 ₃ ¹⁶	2.193; 2.212; 2.205
2.183	3		10 ₁ ¹⁷ ; 10 ₂ ¹⁷	2.178; 2.183
2.165	2		10 ₂ ¹⁸	2.171
2.150	1		10 ₃ ¹⁸	2.156
2.140	3		10 ₁ ¹⁹ ; 10 ₂ ¹⁹	2.133; 2.137
2.132	1		10 ₁ ²⁰ ; 10 ₂ ²⁰	2.133; 2.126
2.116	6		10 ₁ ²¹ ; 10 ₂ ²¹	2.117; 2.115
2.087	4		10 ₁ ²² ; 10 ₂ ²² ; 10 ₃ ²²	2.097; 2.086; 2.078
2.065	2		10 ₂ ²³ ; 10 ₃ ²³	2.073; 2.068
2.037	2	104		
2.018	2		10 ₁ ²⁴ ; 10 ₂ ²⁴	2.008; 2.012
1.998	1		10 ₁ ²⁵ ; 10 ₂ ²⁵	1.996; 2.002
1.984	1		10 ₁ ²⁶ ; 10 ₂ ²⁶	1.984; 1.976
1.950	3		10 ₁ ²⁷ ; 10 ₂ ²⁷	1.952; 1.946
1.865	1		10 ₂ ²⁸	1.867
1.856	2		10 ₁ ²⁹ ; 10 ₂ ²⁹	1.860; 1.860
1.827	8	105		
1.799	4		10 ₁ ³⁰ ; 10 ₂ ³⁰	1.793; 1.798
1.787	1		10 ₁ ³¹	1.786
1.749	2		10 ₁ ³²	1.750
1.730	1		10 ₁ ³³	1.729
1.687	2		10 ₁ ³⁴	1.681
1.677	1		10 ₂ ³⁴	1.674
1.636	6	106		
1.608	4		10 ₁ ³⁵ ; 10 ₂ ³⁵	1.603; 1.609
1.595	4		10 ₁ ³⁶	1.595
1.575	11	110		
1.562	9		111	
1.543	2		10 ₁ ³⁷ ; 11 ₁ ³⁷ ; 11 ₂ ³⁷ ; 11 ₃ ³⁷	1.554; 1.547; 1.536; 1.543
1.526	14	112		
1.512	1		10 ₁ ³⁸ ; 11 ₁ ³⁸ ; 11 ₂ ³⁸ ; 11 ₃ ³⁸	1.513; 1.509; 1.513; 1.515
1.499	2		10 ₁ ³⁹ ; 10 ₂ ³⁹ ; 11 ₁ ³⁹ ; 11 ₂ ³⁹	1.507; 1.502; 1.501; 1.494
1.477	3	107		
1.471	6		113	
1.452	1		10 ₁ ⁴⁰ ; 10 ₂ ⁴⁰ ; 11 ₁ ⁴⁰ ; 11 ₂ ⁴⁰	1.449; 1.452; 1.448; 1.454
1.428	3		10 ₁ ⁴¹ ; 11 ₁ ⁴¹ ; 11 ₂ ⁴¹	1.429; 1.426; 1.431
1.416	2		10 ₂ ⁴² ; 11 ₁ ⁴² ; 11 ₂ ⁴² ; 11 ₃ ⁴²	1.419; 1.419; 1.416; 1.416
1.403	5	114		

TABLE II.—*Continued.*

d in Å. (Electron Diffraction Results Reduced to $(d_{110}) = 1.575$ Å.)	Number of Diffractions Measured.	Indices of Normal Diffractions in Agreement with X-rays.	Possible Indices of Anomalous Diffractions.	d in Å. Corresponding to Indices Assigned to the Anomalous Diffractions.
1.393	2		$11\frac{3}{2}^b$	1.389
1.376	1		$11\frac{1}{2}^b$	1.377
1.364	8	200		
1.353	7	201		
1.341	2	108		
1.332	9	202		
1.323	2		115	
1.314	1		$20\frac{3}{2}^b$; $11\frac{3}{2}^b$; $11\frac{3}{2}^b$	1.315; 1.311; 1.313
1.294	13	203		
1.282	3		$20\frac{1}{2}^b$; $20\frac{1}{2}^b$; $20\frac{1}{2}^b$; $11\frac{3}{2}^b$	1.279; 1.283; 1.285; 1.280
1.275	2		$20\frac{1}{2}^b$; $11\frac{1}{2}^b$	1.276; 1.275
1.268	4		$20\frac{1}{2}^b$; $20\frac{1}{2}^b$; $11\frac{3}{2}^b$; $11\frac{3}{2}^b$	1.271; 1.267; 1.269; 1.264
1.259	3		$20\frac{1}{2}^b$; $20\frac{1}{2}^b$; $11\frac{3}{2}^b$	1.259; 1.257; 1.262
1.249	13	116, 204		
1.241	3		$20\frac{3}{2}^b$; $20\frac{3}{2}^b$	1.237; 1.238
1.233	2		$20\frac{1}{2}^b$; $11\frac{3}{2}^b$	1.234; 1.233
1.224	3	109		
1.205	3			
1.192	13	205		
1.183	2		$20\frac{1}{2}^b$; $20\frac{3}{2}^b$; $20\frac{3}{2}^b$; $11\frac{1}{2}^b$	1.179; 1.182; 1.183; 1.185
1.171	3		117	
1.162	2		$20\frac{1}{2}^b$; $20\frac{3}{2}^b$; $11\frac{3}{2}^b$; $11\frac{3}{2}^b$	1.165; 1.159; 1.159; 1.160
1.155	2		$20\frac{1}{2}^b$	1.155
1.148	3		$20\frac{3}{2}^b$; $20\frac{3}{2}^b$; $11\frac{3}{2}^b$	1.149; 1.147; 1.148
1.145	2		$20\frac{3}{2}^b$	1.145
1.138	6	206		
1.132	2		$11\frac{3}{2}^b$	1.129
1.127	2		$11\frac{3}{2}^b$	1.124
1.122	3	1.0.10		
1.106	6		$20\frac{1}{2}^b$	1.106
1.097	9	118		
1.082	3		$20\frac{1}{2}^b$	1.087
1.076	4	207		
1.031	10	120, 119		
		1.0.11		
1.027	4	121		
1.017	10	122		
0.999	12	123		
0.988	1	124		

and many more diffractions extending down to $d = 0.8$ Å.

On partial rotation these distorted crystals yielded patterns of arcs, spots, streaks and faint-banded areas which were similar in type to those previously obtained from graphite.¹⁷

(b) **Patterns from Thin Crystals of Simple Uni-axial Curvature.**—Some nearly colourless or pale yellow flakes supported on two, and sometimes on three, sides by massive material were obtained. Under the microscope, in reflected light, some of these appeared to be curved about only one axis, which was parallel to the cleavage plane. Fig. 4 was obtained from such a crystal which, judging from the elongation of the central hexagon pattern, was evidently so mounted in the camera that the axis of curvature was not normal to the beam.

¹⁷ Finch and Wilman, *Proc. Roy. Soc., A*, 1936, **155**, Pl. 7, Fig. 9.



FIG. 3. —Transmission through distorted MoS_2 flakes. $L = 50$ cm.
[See page 1542.]

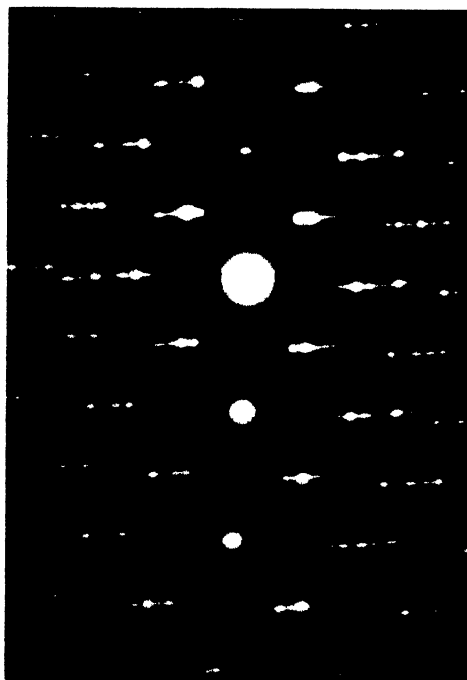


FIG. 4. —Transmission through a uniaxially curved MoS_2 crystal; axis of curvature parallel to cleavage plane, but inclined to beam. $L = 50$ cm.
[To face page 1544.]

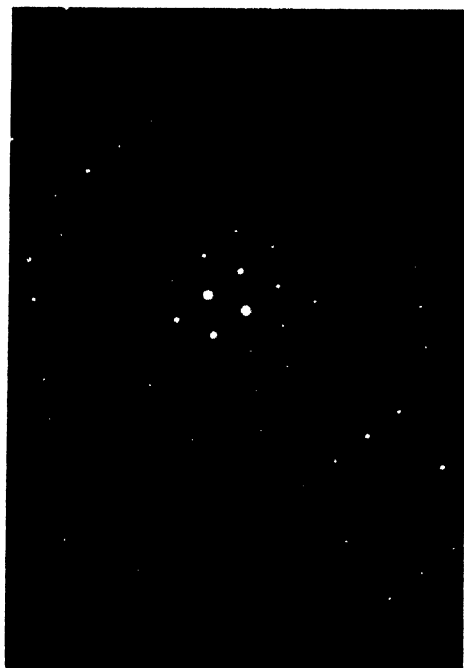


FIG. 5.—Beam nearly normal to cleavage plane of a light olive green MoS_2 crystal. Note faint first Laue order zone. $L = 28$ cm.

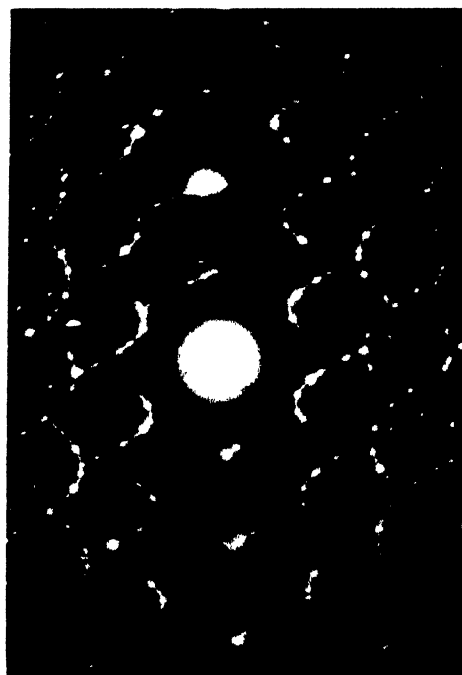


FIG. 6.—Rotation transmission through an undistorted MoS_2 crystal; cleavage plane inclined at 28° to axis of rotation normal to beam. $L = 50$ cm.

[To face page 1545.]

(c) **Diffraction by Thin Undistorted Crystals.**—The thinnest (colourless, or very pale yellow) molybdenite flakes were so sensitive to injury, even by slight air currents, that the only crystals of this thickness which could be mounted in the specimen carrier without distortion or rupture were those which after cleavage spanned a cleft in a thick opaque flake and were thus well supported on at least three sides. Fig. 2 is a sketch of one such specimen which appeared to be quite flat and thus free from distortion when viewed in reflected light under the microscope. With the beam normal to and traversing the light olive-green section it yielded the pure cross-grating pattern, Fig. 5. The corresponding pattern from the yellow and colourless sections were similar, except that being almost entirely free from background they were of remarkable brilliancy and showed no signs of spot intensification, even in the first Laue order region, and were therefore considerably thinner than the light olive-green section. Spot patterns obtained from any of the three thinnest sections with the cleavage plane of the stationary crystal inclined to the beam were similar in type to Fig. 5, except that the hexagonal pattern of spots was elongated in the direction of inclination.

(d) **Rotation Patterns from Undistorted Crystals.**—The above and other undistorted crystals were mounted as accurately as was found practicable with the cleavage plane in the axis of the specimen carrier stem, which was rotated during exposure through a range of up to about 50° on each side of the position where the cleavage plane was normal to the beam. Fig. 4 was obtained, as stated in § 4(b), with a stationary crystal exhibiting simple curvature; but it is also characteristic, in so far as concerns the elongated streaks, of the type of partial rotation pattern recorded with an undistorted crystal mounted with the cleavage plane in the axis of rotation. In further experiments, similar rotation patterns were obtained from these undistorted flakes, the axis of rotation being still normal to the beam and passing through the crystal which, however, had been so mounted that the cleavage plane was inclined more or less steeply to the axis of the carrier. In the case of the patterns Figs. 6 and 7, the cleavage planes were at angles of about 28° and 70° respectively to the axis of rotation.

The spacings of the diffractions visible on several of the streaks in Figs. 6 and 7 agree reasonably well with corresponding values incorporated in Table II. Not only normal but "forbidden" and "fractional order" ("extra") diffractions were also well represented but, owing to the intensity of the streaks and the elongation of the spots produced by tolerance, these relatively weak diffractions do not lend themselves to such accurate measurement as do patterns of the type reproduced in Fig. 3. The corresponding spacing determinations have accordingly not been incorporated in Table II.

(e) **The Effect of Crystal Thickness on the Patterns.**—Figs. 4, 6 and 7 have in common the remarkable feature of continuous lines joining up groups of diffractions. In all these cases the crystals were so thin that little or no signs of Laue zone spot intensification could be detected. These streaks do not appear in otherwise similar patterns from molybdenite specimens which were sufficiently thick to show clear Laue zone effects. Thus in rotation patterns from translucent olive-green crystals, continuous lines were only occasionally faintly visible and were completely absent in the case of the dark olive-green, light brown and still thicker crystals, but became increasingly well-marked on proceeding from the light olive-green to the colourless crystal sections.

5. The Axial Ratio of Molybdenite.

The observed values of the spacings as set forth in Table II. lead to a correspondingly accurate value of the axial ratio of molybdenite in the form of thin crystals. Taking $d_{(110)} = 1.575 \text{ \AA.}$ ¹⁸ and combining with $d_{(101)}$ and $d_{(111)}$, where l is \leq and preferably $> (h + k)$, in order to take advantage

of the greater accuracy of large angle intersections, we obtain in the manner previously described ⁸ the values for c/a as set forth in Table III.

TABLE III.—THE AXIAL RATIO OF MOLYBDENITE IN THE FORM OF THIN CRYSTALS.

$$c/a = \{l^2/[a^2/d_{hkl}^2 - 4(h^2 + k^2 + hk)/3]\}^{1/2};$$

$d_{(110)}$ taken as = 1.575 Å,
i.e., $a = 3.150$ Å.

d in Å.	Indices.	c/a .
2.271	103	3.906
2.037	104	3.891
1.827	105	3.904
1.636	106	3.894
1.477	107	3.903
1.341	108	3.910
1.224	109	3.913
1.122	1.0.10	3.908
1.526	112	3.908
1.403	114	3.918
1.249	116	3.906
1.097	118	3.887

Mean value of $c/a = 3.904$

Hence by electron diffraction the mean value of $c/a = 3.904$ in the thin crystal, compared with 3.905 found by X-rays for the massive substance. Since any appreciable Lennard-Jones effect is most unlikely in the cleavage plane directions, a should be independent of crystal size; we may therefore conclude that the value of c is independent of the crystal thickness, because the X-ray results were obtained with relatively thick crystals.

6. Diffraction by Mica.

Transmission specimens of quite exceptional area could be cleaved from high-grade "ruby" mica of Indian origin, a particularly good batch of which was recovered from a broken-down high-tension condenser. The flakes were picked up on wire frames, lightly smeared with "Seccotine" and suitably shaped to support the crystal from two opposite sides. The appearance of such films and the types of diffraction patterns yielded on trans-

mission are classified for brevity in Table IV.

Although the areas of the largest molybdenite specimens were in general much less than those of the mica films of approximately similar thickness, it will be seen on comparing Tables II. and IV. that what were in all likelihood much the thinnest flakes were obtained from molybdenite. Thus, whilst with molybdenite no great difficulty was experienced in obtaining three grades of thickness decreasing from that giving rise to faint signs of Laue zones, with mica we have only twice succeeded in cleaving and mounting an undistorted crystal exhibiting no first Laue zone effects and of an area sufficiently exceeding the beam cross-section for purposes of rotation.

The rotation patterns yielded by the two thinnest undistorted mica crystals reproduce in all essentials the phenomena observed in the case of molybdenite. Thus the thinnest mica crystal obtained in the course of these experiments gave rise to a pattern recording strongly marked streaks joining families of diffraction spots; when the thickness was such, however, that even faint signs of Laue zones were in evidence the streaks disappeared, although the spots were elongated in the directions which would have been followed by the streaks. To illustrate the results obtained with such a mica crystal and with molybdenite of similar thickness, i.e., olive green in colour, it will suffice to reproduce the pattern, Fig. 8, obtained by partial rotation of a practically undistorted mica crystal about an axis normal to the beam but inclined to the cleavage plane. It is easily seen that, in addition to a slight arcing, the origin of which is discussed in § 7, the diffractions are elongated in the direction of the curves upon which the different groups of spots lie. This is the tolerance effect which, though not then photographically recorded, had previously been described by Finch, Quarrell and Wilman.⁸

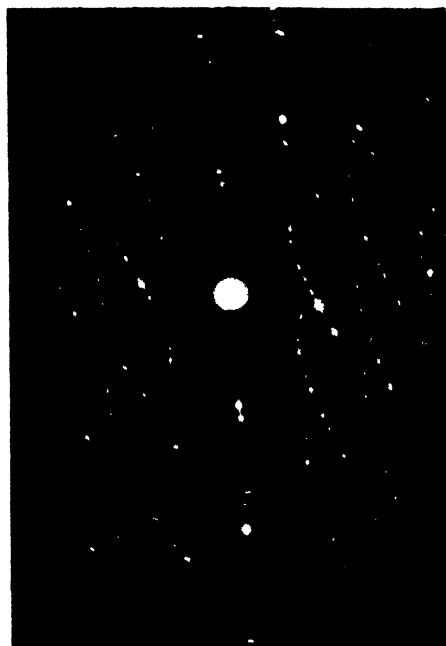


FIG. 7. As in Fig. 6, but inclined at 70° . $L = 50$ cm.
[See page 1545.]



FIG. 8.—Rotation transmission through an undistorted mica crystal with cleavage plane inclined to axis. $L = 28$ cm.
[To face page 1546.]

TABLE IV.—PROPERTIES OF MICA FILMS.

Colour in White Light.			Approximate Area of the Largest Crystal Obtained and Mounted, mm. ²	Type of Diffraction Pattern by Normal Transmission.
Normal Transmission.	Normal Reflection.	Oblique Reflection.		
?	—	—	0.25	No Laue zones.
Pale greyish-blue.	Brownish-yellow.	Golden-yellow.	6	Faint Laue zones.
Pale blue.	Orange-yellow.	—	25	Medium Laue zones.
Pale yellow.	Bright blue.	Brilliant violet.	50	Medium Laue zones; faint Kikuchi lines.
Yellow.	Violet blue.	Magenta red.	—	—
Greenish-blue.	Brownish-yellow.	—	60-80	Strong Kikuchi lines.
Purplish blue.	Olive green.	—	—	—
Pale blue.	Brownish-yellow.	Greenish.	—	—
Green.	Red.	Green.	—	—
Pale green.	Pale red.	Green.	500	Pattern wholly or nearly submerged in general background.
Pale blue.	Pale-yellowish-brown.	—	—	—
Pale blue.	Yellowish green.	—	—	—

7. Discussion.

In addition to spectra which are normal in that they agree with those obtained with X-rays, many anomalous diffractions from molybdenite have been observed and are recorded in Table II.

Turning to Figs. 4, 6 and 7, in which the streaks are such prominent features of the patterns, we observe in the first place that these all pass through related series of diffractions and, indeed, that no isolated diffractions are to be found elsewhere than on the streaks and, since some of the spots on the streaks are anomalous diffractions, it follows that this fact by itself, like others previously recorded,⁸ renders untenable any explanation of the "extra" diffractions in terms of impurities.

By postulating a slipping of cleavage planes into irregular alternations of the two possible close-packing arrangements of neighbouring layers, brought about by the operation of shearing forces during cleavage of a thin molybdenite crystal, we can conceive of a stable structure being formed which has no true unit cell. Such a structure would continue to give the normal cross-grating type of pattern at any setting, but whilst the diffracted rays from some of the superposed cross-gratings would reinforce to yield all possible diffractions of the normal unit cell of integral h , k and l values, both normal and forbidden by structure factor,

others would give rise to anomalous diffractions in positions corresponding, for the normal unit cell, to fractional l index values. Several facts, however, appear to negative any such explanation of the origin of the anomalous diffractions. In the first place, it would seem most unlikely that such slipping could have occurred in an undistorted crystal flake securely supported on three sides, as shown in Fig. 2. Furthermore, one would reasonably expect such slipping either to change substantially the value of the axial ratio as a whole or to make it indefinite, which is contrary to what has been set forth in § 5. Finally, the facts relating to the thickness of the crystals examined lead to a further cogent argument against the supposition of slip distortion of the crystal as being responsible for the anomalous diffractions. Thus, with the light olive-green flakes, the breadth of the Laue zero order suggested a thickness of about 40 Å. though, owing to the possibility of a pronounced double scattering, this may be somewhat of an underestimate. Since, however, three lesser grades of thickness than this have been obtained, it is almost certain that the thinnest, practically transparent crystals cannot have been more than three or four layers thick. Hence, no matter what slip-distortion into close-packing (and any other arrangement would be either metastable or unstable) be postulated, it does not seem possible with so few layers to account for more than a few of the anomalous diffractions in this way.

We are thus driven to fall back upon the view previously advanced in explanation of the anomalous diffractions encountered in the case of graphite.⁸ Such diffractions fall into two groups. Integral indices have been assigned to the one group, conveniently termed "forbidden" diffractions, in the sense that their occurrence conflicts with the structure factor considerations as normally derived from the massive crystal, *i.e.*, a space lattice extending virtually to infinity in all directions. Thus the normal structure amplitude, S , is given by

$$S = A = \overline{M}_0 [2 \cos \pi(h + k + l) \cdot \cos \pi(h/3 - k/3 + l/2)] \\ + \overline{S} [2 \cos \pi(h + k) \cdot \cos \pi(h/3 - k/3 - 2ul) \\ + 2 \cos \pi(h + k + l) \cdot \cos \pi(h/3 - k/3 + 2ul)],$$

where \overline{M}_0 and \overline{S} are the scattering powers of the molybdenum and sulphur atoms respectively, because B , the term involving the sines, is clearly always zero. Hence for $11l$ type diffractions we have

$$A = \overline{S} \cdot 2 \cos 2\pi ul [1 + \cos \pi(l + 2)].$$

Thus the 111 , 113 , 115 , etc., diffractions are forbidden and do not occur with the massive crystal. The fact that they do, however, appear in our electron diffraction patterns from very thin crystals is reasonably explained in terms of the limitation of the lattice, and hence of incompletely developed periodicities, in directions other than those of the cleavage plane resulting in relaxation of the structure factor restrictions. It is quite possible, and indeed likely, that double scattering also contributes to the intensity of the "forbidden" diffractions.^{9, 16, 18, 19, 20}

The occurrence of the second kind of anomalous diffraction, conveniently termed "extra" or "fractional order," is also to be accounted for in terms of the same theory. In this case, however, though double

¹⁸ Raether, *Z. Physik*, 1932, **78**, 527.

¹⁹ Shinohara, *Physic. Rev.*, 1935, **47**, 730.

²⁰ Beeching, *Phil. Mag.*, 1935, **20**, 841.

scattering may still affect the intensities of the "extra" diffractions by tending to even out the intensity distribution, it cannot of course in any way lead to their formation.

The considerations leading to the derivation of the fractional order indices for molybdenite are again based on the theorem,

$$uh + vk + wl = 0,$$

where u , v , w , are not only the indices of a zone axis to which the (hkl) plane belongs, but are also possible values of the beam indices when fast electrons are being diffracted by the corresponding family of parallel net planes; u , v , w , h and k can have any integral values, irrespective of whether l thereby becomes fractional or otherwise, because, owing to the thinness of the crystal, the lattice is limited in the l direction, but is of virtually unlimited extent in the h and k directions. The indices, h and k , define the intersection of (hkl) with the cleavage plane; both must be integral for (hkl) to pass through atom rows in the cleavage plane, and must be small for these to be main rows. By assigning a range of probable values to u , v , w , h and k , we can identify the atom rows in a diffracting plane family which must be parallel to the beam to give rise to any particular "extra" diffraction but, owing to the fact that the lattice limitation in the c direction, *i.e.*, the flake crystal thickness, is not known accurately, it is difficult to allow even qualitatively for the influence of the structure factor of the limited lattice upon the intensity of the fractional order diffractions. Hence, and bearing in mind also the added uncertainty introduced by double scattering, we consider it prudent not to rely on the relative intensities of the "extra" diffractions, but find that the theoretical spacings calculated from the indices arrived at in the above-outlined manner agree so satisfactorily with the experimentally determined spacings of the recorded fractional order diffractions as to afford further strong support of the theory of the origin of fractional orders as first put forward in the case of graphite.

From Table II. it will be seen that a series of anomalous diffractions, all lying within the 100 diffraction, still remain unexplained. Like the other "extra" and "forbidden" diffractions, however, they cannot be ascribed to impurities because they are not sporadic, but are a characteristic feature of all patterns so far obtained from strongly distorted; extremely thin molybdenite crystals. On the other hand, we have never observed these innermost extra diffractions with undistorted crystals, even on rotation. Thus it would seem that these innermost diffractions are in some way connected with changes brought about in the diffraction conditions or in the lattice by the extreme degree of distortion represented by crinkling.

With regard to the origin of the streaks, it has been already noted that they pass through families of diffractions. Furthermore, it has also been pointed out that in rotation patterns they are prominent only when the crystals are very thin, and that with increasing thickness they become weaker. Hence we interpret these streaks as the result of a space lattice limitation in the beam direction which has proceeded nearly to the lowest possible limit, *i.e.*, one layer in thickness. A single cleavage layer of molybdenum sulphide molecules would on rotation behave essentially like a true cross-grating and give practically continuous diffraction lines. The fact, however, that diffraction spots do appear on even the most intense streaks, shows that the thinnest crystals must have been at least two layers thick.

The sharpness of the streaks, as shown for example in Figs. 4, 6 and 7, is proof of the perfection of the atomic lattice in each sheet and of the exact similarity of the hexagonal arrangement in all the sheets of the crystal, even in the thinnest flakes so far obtained.

The occurrence of the prominent two-dimensional diffraction streaks in patterns from very thin rotated undistorted, and from curved stationary single crystals which we have now recorded in Figs. 4, 6 and 7 and the extension of the spots in Fig. 8 confirm the existence of the tolerance effect previously noted by us.² Darbyshire and Cooper's³ failure to repeat those observations with a curved crystal is now seen clearly to have been due to its having been too thick. The elongation of the spots and the direction in which it occurs is such as to establish the existence of a pronounced tolerance effect, even with a crystal which was actually sufficiently thick to show well-marked, though rather broad Laue zone effects, and which was therefore too thick to give rise to continuous streaks on rotation. With still thinner crystals the effect of tolerance becomes even more pronounced; the arrows point in Fig. 4 to a streak of high and uniform intensity and about 3 mms. long.

That such pronounced tolerance effects can and do arise in the case of thin crystals must have important effects on patterns from random crystal aggregates and more particularly from polycrystalline specimens exhibiting one degree of orientation. Thus, for example, rotation of the pattern, Fig. 4, about the beam would give rise to a series of circular bands with more or less well-defined limits swept out by the streaks, and to rings of an abnormal breadth. This last phenomenon introduces an additional uncertainty into the problem of the estimation of particle size from ring-broadening, though it may be pointed out that when this is due to tolerance it takes place outwards, whilst broadening due to particle size of stationary crystals must occur practically symmetrically about the normal ring position.

The dark, so-called "extinction" ring previously observed²¹ with a polycrystalline mica specimen may well be due to the close approach of the outer head of an inner band swept out by a streak family to the inner head of a similar band but of larger diameter.

The peculiar curvature of the streaks obtained from undistorted crystals rotated about an axis inclined to the cleavage plane, can be accounted for quantitatively. The problem is to determine the loci of the intersections with the screen of rays diffracted from a rotating plane cross-grating. We will first consider the perfectly general case of the grating inclined to the axis of rotation which itself may be at any angle to the beam, as follows:—

In the reciprocal lattice construction for the directions of the diffracted beams, the pure cross-grating crystal lattice is represented by a system of continuous parallel lines passing through points of the normal reciprocal lattice of the true three-dimensional crystal which lie on rows normal to the plane of the cross-grating. The directions of the diffracted beams are then obtained in the usual way by joining the points of intersection of each of these lines with the Ewald "sphere of reflection," of reciprocal wave-length radius, to its centre at this distance, *i.e.*, $1/\lambda$, from the origin of the reciprocal lattice and in the direction of the beam source. In view of the short electronic wave-length and the small angles of diffraction, the section of the sphere involved may with sufficient accuracy

²¹ Finch, Quarrell and Wilman, *Trans. Faraday Soc.*, 1935, 31, Pl. 13, Fig. 35

be regarded as plane. In the present case of molybdenite the cross-grating is a (001) plane of atoms, and a particular ($h k$) line of its reciprocal lattice is represented by the line PL (Fig. 9) distant r from the origin O of the lattice; PL and ON are normal to the cross-grating plane. Suppose the electron beam direction be along ZO (Fig. 10) and the axis of rotation of the crystal be OY_1 , making an angle $(90 - \delta)$ with ZO . Take as three orthogonal co-ordinate axes the directions OZ and OY in the plane of OZ and OY_1 , and OX perpendicular to OZ and OY . The Ewald sphere of reflection is then represented by the OXY plane, tangent to it at the origin O , and we require the locus of the point of intersection of the line PL with the plane OXY as PL rotates with the cross-grating about the axis OY_1 .

Let the cross-grating normal ON be inclined at an angle ξ to the axis of rotation OY_1 . Take another set of orthogonal axes formed by OX_1 along OX , OY_1 , and OZ_1 perpendicular to OX_1 and OY_1 , and consider

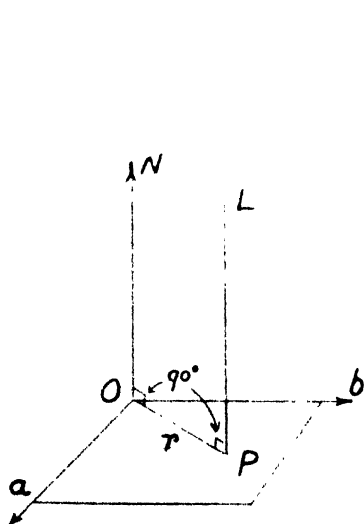


FIG. 9.

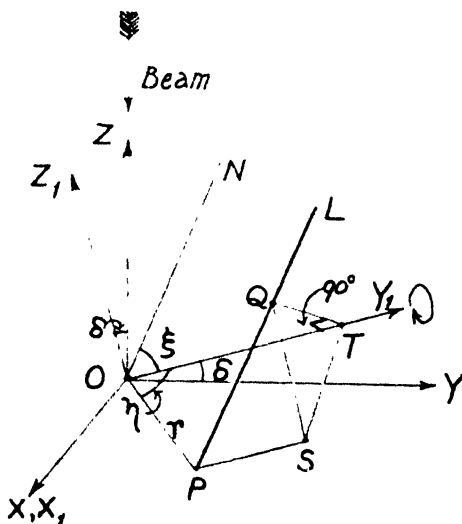


FIG. 10.

the position of the cross-grating in which OP , the perpendicular from O to the ($h k$) reciprocal lattice line, lies in the $OX_1 Y_1$ plane at an angle η to OY_1 . The values of ξ , η , δ and r are constant for a given ($h k$) line and a given orientation of the rotation axis relative to the cross-grating and to the beam direction.

P has co-ordinates $(r \sin \eta, r \cos \eta, 0)$, and the direction cosines of OP with respect to $OX_1 Y_1 Z_1$ are equal to $(\sin \eta, \cos \eta, 0)$. The line PL passes through P and, if its direction cosines are (u, v, w) , its equation with respect to $OX_1 Y_1 Z_1$ is

$$\frac{x_1 - r \sin \eta}{u} = \frac{y_1 - r \cos \eta}{v} = \frac{z_1}{w} = d \quad . \quad . \quad (1)$$

whence $d^2 = x_1^2 + y_1^2 + z_1^2 + r^2 - 2x_1 r \sin \eta - 2y_1 r \cos \eta$.

Thus the co-ordinates (x_1, y_1, z_1) of any point Q on PL must satisfy these relations, and the distance from P along PL to Q is d . The values of

(u, v, w) are given by the relations

$$\left. \begin{aligned} u \sin \eta + v \cos \eta &= 0, \\ v &= \cos \xi, \\ u^2 + v^2 + w^2 &= 1; \end{aligned} \right\} \quad . \quad . \quad . \quad (2)$$

and the first expressing the fact that PL is perpendicular to OP , and the second that PL always makes an angle ξ with OY_1 . Hence

$$\left. \begin{aligned} u &= -\cos \xi \cot \eta, \\ v &= \cos \xi, \\ w &= \{1 - (\cos^2 \xi / \sin^2 \eta)\}^{\frac{1}{2}} \end{aligned} \right\} \quad . \quad . \quad . \quad (3)$$

The co-ordinates of Q are, from (1),

$$\left. \begin{aligned} x_1 &= ud + r \sin \eta, \\ y_1 &= vd + r \cos \eta, \\ z_1 &= wd. \end{aligned} \right\} \quad . \quad . \quad . \quad (4)$$

On rotation of the cross-grating and its associated reciprocal lattice lines about OY_1 , the point Q moves round a circle of centre T on OY_1 , where QT is perpendicular to OY_1 and of length r_1 , so that

$$x_1^2 + z_1^2 = r_1^2, \quad . \quad . \quad . \quad (5)$$

where r_1 is a function of y_1 . The line PL always lies in the surface of a hyperboloid of revolution round OY_1 , whose equation is obtained by finding the value of r_1 in (5) by substitution of x_1 and z_1 from (4), followed by elimination of d in terms of y_1 from the second equation of (4). The equation of the hyperboloid with respect to $OX_1Y_1Z_1$ is thus

$$(x_1^2 + z_1^2) \cos^2 \xi - y_1^2 \sin^2 \xi + 2y_1 r \cos \eta - r^2 (\cos^2 \xi + \cos^2 \eta) = 0, \quad (6)$$

and the locus of the point of intersection of PL in OXY is clearly the curve of intersection of this hyperboloid with the plane OXY . This curve, like any intersection of a quartic with a plane, is a conic.

For the transformation of the axes from $OX_1Y_1Z_1$ to $OXYZ$ we have the relations,

$$\left. \begin{aligned} x_1 &= x, \\ y_1 &= y \cos \delta + z \sin \delta, \\ z_1 &= -y \sin \delta + z \cos \delta \end{aligned} \right\} \quad . \quad . \quad . \quad (7)$$

The hyperboloid referred to $OXYZ$ now has the equation

$$\begin{aligned} (x^2 + y^2 \sin^2 \delta - 2yz \sin \delta \cos \delta + z^2 \cos^2 \delta) \cdot \cos^2 \xi - (y^2 \cos^2 \delta \\ + 2yz \sin \delta \cos \delta + z^2 \sin^2 \delta) \cdot \sin^2 \xi + 2r \cos \eta (y \cos \delta + z \sin \delta) \\ - r^2 (\cos^2 \xi + \cos^2 \eta) = 0, \end{aligned}$$

and its intersection with the OXY plane, $z = 0$, is

$$\begin{aligned} x^2 \cos^2 \xi + y^2 (\sin^2 \delta - \sin^2 \xi) + 2yr \cos \eta \cos \delta \\ - r^2 (\cos^2 \xi + \cos^2 \eta) = 0 \end{aligned} \quad (8)$$

Transfer the origin to the centre O' (x_0, y_0) of this conic; then equation (8) becomes

$$\begin{aligned} (x + x_0)^2 \cos^2 \xi + (y + y_0)^2 \cdot (\sin^2 \delta - \sin^2 \xi) \\ + 2(y + y_0) r \cos \eta \cos \delta - r^2 (\cos^2 \xi + \cos^2 \eta) = 0, \\ \text{i.e., } x^2 \cos^2 \xi + y^2 (\sin^2 \delta - \sin^2 \xi) + 2xx_0 \cos^2 \xi + 2y[y_0 (\sin^2 \delta \\ - \sin^2 \xi) + r \cos \eta \cos \delta] + x_0^2 \cos^2 \xi + y_0^2 (\sin^2 \delta - \sin^2 \xi) \\ + 2y_0 r \cos \eta \cos \delta - r^2 (\cos^2 \xi + \cos^2 \eta) = 0. \end{aligned}$$

For (x_0, y_0) to be the centre, the coefficients of x and y must vanish. Therefore,

$$x_0 = 0; \quad \text{and} \quad y_0 = -r \cos \eta \cos \delta / (\sin^2 \delta - \sin^2 \xi) \quad (9)$$

The equation referred to the centre O' as origin is thus:—

$$x^2 \cos^2 \xi + y^2 (\sin^2 \delta - \sin^2 \xi) - r^2 [\cos^2 \xi + \cos^2 \eta + \cos^2 \eta \cos^2 \delta / (\sin^2 \delta - \sin^2 \xi)] = 0,$$

$$\text{i.e.,} \quad \frac{x^2}{\frac{r^2}{\cos^2 \xi} \left(\cos^2 \xi + \cos^2 \eta + \frac{\cos^2 \eta \cos^2 \delta}{\sin^2 \delta - \sin^2 \xi} \right)} + \frac{y^2}{\frac{r^2}{\sin^2 \delta - \sin^2 \xi} \left(\cos^2 \xi + \cos^2 \eta + \frac{\cos^2 \eta \cos^2 \delta}{\sin^2 \delta - \sin^2 \xi} \right)} = 1 \quad (10)$$

This is, in general, an ellipse or a hyperbola according to whether $(\sin^2 \delta - \sin^2 \xi)$ is positive or negative, i.e., $|\delta|$ is $>$ or $<$ $|\xi|$, since $0 < \xi < 90^\circ$, and $-90^\circ < \delta < +90^\circ$.

In the case of our undistorted single crystal rotation experiments, the axis of rotation OY_1 is normal to the beam (OZ), so that $\delta = 0$; thus, the locus of the hk intersection with the plane OXY is given by:—

$$\frac{x^2}{\frac{r^2}{\cos^2 \xi} (\cos^2 \xi + \cos^2 \eta - \cos^2 \eta / \sin^2 \xi)} - \frac{y^2}{\frac{r^2}{\sin^2 \xi} (\cos^2 \xi + \cos^2 \eta - \cos^2 \eta / \sin^2 \xi)} = 1 \quad (11)$$

If $(\cos^2 \xi + \cos^2 \eta - \cos^2 \eta / \sin^2 \xi) = 0$, i.e., $\sin^2 \xi - \cos^2 \eta = 0$, i.e., $(90^\circ - \xi) = \eta$, then this locus reduces to a pair of straight lines with the equations, $y = \pm x \cot \xi$. In all other cases, the locus is always a hyperbola (e.g., Fig. 11), whose centre O' lies on the axis OY at a distance $r \cos \eta / \sin^2 \xi$ from the origin O , and whose axis is parallel to either OX or OY according to whether $(\sin^2 \xi - \cos^2 \eta)$ is positive or negative, i.e., whether $(90^\circ - \xi)$ is $>$ or $<$ η . Since the centre of the hyperbola is on the co-ordinate axis OY , i.e., the projection of the rotation axis, the hyperbolæ for which $(90^\circ - \xi)$ is $<$ η must all have OY as their common axis, and therefore form a small coaxial group which should be, and are indeed, recognisable in the diffraction patterns. The equations of the asymptotes are $y = \pm x \cot \xi$, referred to the centre O' as origin. If the axis of the hyperbola is parallel to OX

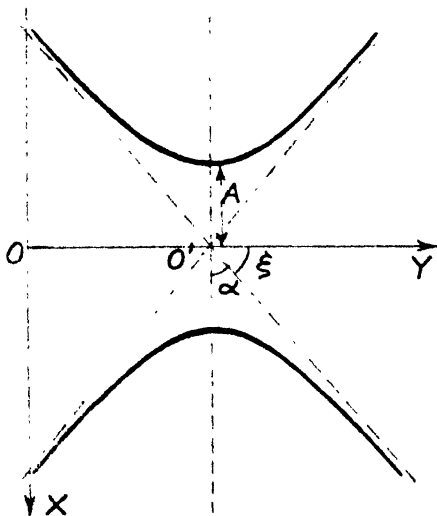


FIG. 11.

the length, A (Fig. 11), of the semi-axis of the hyperbola is

$$\{r^2 (\cos^2 \xi + \cos^2 \eta - \cos^2 \eta / \sin^2 \xi) / \cos^2 \xi\}^{\frac{1}{2}} = r(1 - \cos^2 \eta / \sin^2 \xi)^{\frac{1}{2}};$$

or if the axis of the hyperbola is along OY then the semi-axis is

$$r \cos \xi (\cos^2 \eta - \sin^2 \xi)^{\frac{1}{2}} / \sin^2 \xi.$$

Let the wave-length of the electrons be λ and the camera-length L with the photographic plate perpendicular to the beam, then the actual locus of the hk diffraction spot on the plate will be the above hyperbola magnified in the ratio of $L\lambda:1$. A typical rotation photograph would therefore consist of a large number of such hyperbolic traces, nearly all with their axes parallel to OX and their centres on the projection of the axis of rotation; furthermore, the asymptotes of all these hyperbolæ will enclose the same angle 2α (Fig. 11), where $\alpha = (90^\circ - \xi)$, i.e., α is the angle of inclination of the cross-grating to the axis of rotation. Therefore, when the rotation axis is nearly parallel to the cross-grating plane, the hyperbolæ will be acute, as in Fig. 6, and when actual parallelism occurs, i.e., $\xi = 90^\circ$, the hyperbolæ will have shrunk to a set of parallel straight lines given by $y = r \cos \eta$ with respect to O as origin and beginning at the points $x = \pm A, = \pm r \sin \eta$, corresponding to the apices of the hyperbolæ. Since simple curvature about an axis parallel to the cleavage plane is clearly equivalent to rotation of a plane crystal about that axis, Fig. 4 will serve to illustrate the fact that the hyperbolæ also become parallel straight lines when the axis of rotation is parallel to the cross-grating plane but not perpendicular to the beam, i.e., when $\xi = 90^\circ$, but $\delta \neq 0$.

In the general case, when $\xi \neq 90^\circ$ and $\delta \neq 0^\circ$, the hk hyperbolic or elliptic locus in the OXY plane has its centre O' at the point with the co-ordinates 0 and $-r \cos \delta / (\sin^2 \delta - \sin^2 \xi)$; the asymptotes of the hyperbolæ with respect to O' as origin are the lines,

$$y = \pm x \cos^2 \xi / (\sin^2 \xi - \sin^2 \delta);$$

and the semi-axis is of length

$$r[1 + \cos^2 \eta / (\sin^2 \delta - \sin^2 \xi)]^{\frac{1}{2}}.$$

If the locus is an ellipse the denominators of the x^2 and y^2 terms in equation (10) are the squares of the semi-axes, which are parallel to OX and OY .

In the case where the axis of rotation is the normal to the cross-grating, $\xi = 0$, and arbitrarily taking $\eta = 90^\circ$, the locus of the hk diffraction is

$$x^2/r^2 + y^2/(r^2/\sin^2 \delta) = 1 \quad . \quad . \quad . \quad (12)$$

The hk loci are thus all ellipses with O as centre, with the major axes in the direction OY and minor axes along OX , the semi-axes being of length r and $r/\sin \delta$. Such ellipses have actually been observed in the case of transmission patterns obtained from orientated polycrystalline films of cadmium iodide²² and from colloidal silver.²³ The arcs, or rather spots, of hkl diffractions from an orientated polycrystalline specimen must lie on the corresponding hk ellipse, as in the case of a transmission pattern from an orientated colloidal graphite specimen inclined to the beam.²⁴

The rotation of a cylindrically-curved cross-grating about any axis other than that of the curvature clearly results in the alteration in

²² Kirchner, *Ergeb. exakt. Naturw.*, 1932, 11, 64.

²³ Finch, Quarrel and Wilman, *Trans. Faraday Soc.*, 1935, 31, Pl. 11, Fig. 27.

²⁴ Finch and Wilman, *Proc. Roy. Soc., A*, 1936, 155, Pl. 6, Fig. 2.

position and shape of the hyperbolic loci of the stationary cross-grating, so that each hk hyperbola on the photographic plate sweeps out a corresponding area throughout which diffuse diffraction effects will be recorded. Usually the crystals, e.g., of molybdenite, are at least thick enough to show more intense spots where each streak crosses the appropriate normal hkl Debye-Scherrer ring positions for the three-dimensional lattice powder-pattern; hence rotation of such a bent flake about any axis will yield well-marked arcs of the normal Debye-Scherrer ring pattern superimposed on areas of diffuse diffraction. This phenomenon has previously been observed with graphite flakes,¹⁷ and we have furthermore been able to infer the existence of a very slight curvature in some otherwise apparently quite flat flakes of molybdenite and mica from their tendency to yield patterns of short arcs instead of spots in those parts of the rotation patterns corresponding to high inclination of the specimen plane to the beam. Indeed, we have in this phenomenon a delicate test for the absence or otherwise of curvature, whether macroscopic or of the lattice-type recently postulated by Lotmar.²⁵ As stated above in § 4 (*d*), the crystal yielding Fig. 7 appeared under the microscope to be quite flat in reflected light; the distinct signs of arcing visible in the case of the diffractions remote from the central spot and corresponding to large inclinations of the cleavage plane to the beam show, however, that the flake in question must have been very slightly curved.

In the above analysis the diffraction loci given by equation (10) are those of a pure cross-grating. In the case of a crystal of finite thickness the hkl diffractions must occur on these loci, because the cross-grating reciprocal lattice lines pass through the points of the normal reciprocal lattice rows of the three-dimensional lattice. The ool diffractions would appear on a pair of straight lines intersecting in the central spot. Thus in the case of these diffractions, the ool reciprocal lattice points must lie on the oo cross-grating reciprocal lattice line, and the intersection of this line with the Ewald sphere is therefore to be obtained by putting $r = 0$ in equation (10). Hence

$$y = \pm x \cos \xi / (\sin^2 \xi - \sin^2 \delta)^{\frac{1}{2}}, \quad . \quad . \quad . \quad (13)$$

Thus when $|\xi|$ is $> |\delta|$, i.e., the h, k curves are ellipses, the ool diffractions will not appear; when $|\xi|$ is $< |\delta|$, i.e., the h, k curves are hyperbolæ, the ool diffractions should lie on the above lines which are parallel to the asymptotes of the h, k hyperbolæ and pass through the central spot. In view of the thinness of the crystals and their virtually infinite extent in the cleavage plane directions, it is not surprising that these diffractions do not appear in the patterns from either curved or rotated undistorted single crystals of molybdenite. As in the case of graphite, the ool diffractions are conspicuous by their absence.

Finally, we have obtained patterns of strongly-curved intense streaks of the type shown in Figs. 6 and 7 from stationary molybdenite crystals. Their origin can now be explained simply in terms of polyaxial curvature.

Summary.

The diffraction of electrons by thin stationary and rotating molybdenite crystals has been studied. The principal facts and conclusions arrived at are as follows:—

²⁵ Lotmar, *Z. Krist.*, 1936, 91, 187.

In addition to those to be anticipated from the known structure, many anomalous diffractions have been recorded and explained in terms of the lattice limitation theory, as first applied to the graphite spectra.

Single crystals of only a few lattice layers in thickness, some free from distortion and others exhibiting only simple uniaxial curvature, have been obtained and have yielded on rotation the two-dimensional cross-grating effect of continuous diffraction lines. It has been shown that such lines, and tolerance effects in general, decrease in intensity with increasing crystal thickness. Such tolerance effects have also been recorded with mica.

As with X-rays, the axial ratio of molybdenite has been found to be 3.90, from which it is concluded that c is independent of crystal thickness.

The general theory of the loci of the diffractions from rotating undistorted and from stationary curved molybdenite crystals has been developed and shown to be in agreement with experiment.

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THE REFRACTIVE INDEX OF DEUTERIUM.

BY W. J. C. ORR.

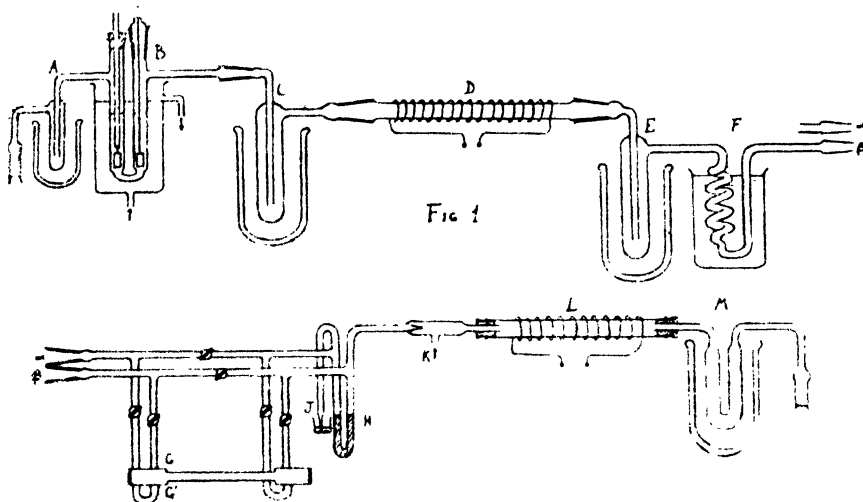
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A property of deuterium which has so far not been determined is its refractive index. The present experiments were undertaken to determine the difference in refractivity of hydrogen and deuterium at constant temperature and pressure, the gases being compared simultaneously in the gas tubes of a Rayleigh Interferometer. A further consideration was that, if there were a large difference in refractive index such measurements would offer a convenient method of analysing hydrogen-deuterium mixtures. As will appear however, the difference was very small so that with the instruments used the analytic accuracy of this method was limited to ± 1.0 per cent. D.

Apparatus.

The apparatus employed is shown diagrammatically in Fig. 1. The portion from A to F was made in duplicate and the two pieces coupled together so that the hydrogen liberated in one electrolytic cell and the deuterium in the other underwent identical treatments before entering the opposite sides of the Interferometer gas tubes at G and G'. The U-shaped cells, B, were narrowed at the bend to permit as much electrolyte as possible being electrolysed, and were fitted with platinum electrodes of $\frac{1}{4}$ sq. cm. area, the cathodes being attached to stout platinum wires, sealed in ground glass joints. The tubes D, in which traces of oxygen were combined with hydrogen were of pyrex glass and were filled with platinised asbestos and electrically heated so that a temperature of 250-300° C. was maintained inside. The traps, C, were cooled in liquid air and those at E, by ether-CO₂ mixtures. In order that the gases might

be at room temperature when entering the gas tubes, spirals immersed in water, were placed at F. The two streams leaving the gas tubes were led to the opposite limbs of a mercury manometer, H, by which any difference in their pressure was immediately detected, the hydrogen then passing into the atmosphere through the constriction, J, which just touched



a mercury surface, while the deuterium passed to the CuO tube, L, which was kept at 500°C . by an electric furnace. The heavy water so produced was frozen out in the U-tube, M, cooled in an ether- CO_2 mixture and so recovered. The volume of each side of the apparatus from C to H was approximately 300 c.c.

Experimental and Results.

The cells, filled first of all with ordinary water to which a little NaOH had been added, were connected in series and electrolysed at a current of 1 amp. for 6 hours. The heating coils at C, were not put on till after 3 or 4 hours so that the apparatus was filled with hydrogen without risk of explosion. During this run the zero reading on the interferometer with ordinary hydrogen in both sides of the gas tubes was determined, while in addition, it was ascertained that no leakage took place through the rubber tubing connecting the gas tubes to the apparatus and also, it was found that a correct reading of the Interferometer could be made while the gases were streaming through the tubes.

A 3*N* NaOH solution in 99.1 per cent. D_2O was now placed in one of the cells and electrolysis with a current density of 0.6-1.0 amps. commenced. The following tables show the course of the readings as the experiment progressed.

(1) 3 c.c. DOD used.

Hours	0	3	4	5	1.0 c.c. DOD added	9
Drum divisions	0	22.8	24.8	27.0		27.0

(2) 2.2 c.c. DOD were then added to the alkali left after the above experiment and the following readings were obtained :—

Hours . . .	3	4	6	10	16	20	22
Drum divisions .	22.8	30.0	34.5	35.0	35.0	35.0	35.0

It is evident that all the initial H_2 must be swept out after 19 hours evolution of D_2 at a rate of 250 c.c per hour. Furthermore it is easily calculable from the volumes of the solutions and the known original D concentration, assuming as low a separation factor as 4, that after 19 hours electrolysis at least 99.9 per cent. D_2 is being liberated. It may thus be concluded that the final reading represents the fringe displacement (given in drum divisions corresponding to pure D_2). As a check the D concentration of the liquid left in the cell was analysed by density measurements and found to be 99.9 ± 0.2 per cent. D.

The difference between the refractive indices of hydrogen and deuterium ($\Delta\mu$) corresponding to an interferometric shift of 35.0 drum divisions is given by the formula :

$$\Delta\mu = \frac{N\lambda}{L} \times 10^{-8},$$

where N is the number of fringes corresponding to a shift of 35.0, when a monochromatic light source of wavelength, λ Å. is used ; and L is the length of the gas tubes, *viz.*, 75 cms. The correction which, in general, would be applied to this formula to take account of dispersion is completely negligible in this case where a shift of less than two fringes is involved.

The calibration of the drum reading was made using the wave-length 5462 Å., suitably filtered from a mercury arc source. The following readings were obtained for consecutive fringes :—

	934.0	948.2	962.1	976.5	991.1
Difference	14.2	13.9	14.4	14.6	
Average difference = 14.2 (5).					

Hence

$$N = \frac{35.0}{14.25} \therefore \Delta\mu = \frac{35.0}{14.25} \times \frac{5462}{75} \times 10^{-8} = (179 \pm 2) \times 10^{-8}.$$

From the design of the instrument a shift in the direction observed, indicated that deuterium had a smaller refractive index than hydrogen. The refractive index of H_2 at λ 5462, given by the Int. Crit. Tables is 1.00013966 (273 Å., 760 mm.).

Hence the refractive index of deuterium under the same conditions is 1.0001378(7).

Summary.

The difference in the refractive indices of hydrogen and deuterium have been determined, using a Rayleigh Gas Interferometer. Assuming the value 1.00013966 for hydrogen at λ 5462 the refractive index of deuterium is found to be 1.0001378(7).

I wish to thank Dr. J. A. V. Butler for suggesting this investigation and for his encouragement during the course of the work. I have also to express my gratitude to the Carnegie University Trust for a Scholarship, to the Moray Fund for a grant for the purchase of heavy water, and to Messrs. Imperial Chemical Industries for a grant by which the Interferometer was purchased.

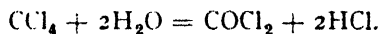
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DISCONTINUITIES IN THE SORPTION PROCESS.

BY A. G. FOSTER.

Received 5th August, 1936.

It has been shown by Burrage¹ that when a silica gel containing adsorbed carbon tetrachloride vapour is heated to about 100° C., a chemical reaction occurs which results in the removal of some of the residual water of the gel. The action is presumably similar to that which is known to take place on moist charcoal,



and the removal of water is accompanied by a marked change in the shape of the sorption isothermals. Those determined on a gel which has not been subjected to any "flushing out" treatment are of normal type and show no discontinuities,² whilst those determined after treatment, the gel being completely evacuated and recharged, show a definite step-like structure, in which the pressure remains constant over a certain range of concentration and then falls abruptly to a lower value, also remaining constant for a time. Similar curves have been obtained by Burrage,³ using the dynamic retentivity method, without any preliminary treatment of the gel.

During the examination of a silica gel by the dynamic retentivity method discontinuities were also observed by the author, but subsequent examination by a static method not only failed to reveal any regular discontinuities, but showed also that the true shape of the curve was considerably different from that determined by the air-stream (dynamic) method. Isothermals of several alcohols on this gel have been described previously by the author.⁴ All show a small hysteresis loop (just before the saturation point is reached), in the "descending" branch of which, slight discontinuities have been found. At lower concentrations however, a most careful examination of all the isothermals failed to reveal any marked discontinuities. The same behaviour has been found in the present work with carbon tetrachloride, on the same gel, since the isothermals show a few breaks in the hysteresis

¹ Burrage, *J. Physic. Chem.*, 1933, **37**, 735.

² Allmand and Burrage, *Proc. Roy. Soc., A*, 1931, **130**, 610.

³ Burrage, *J. Physic. Chem.*, 1933, **37**, 33.

⁴ Foster, *Proc. Roy. Soc., A*, 1934, **146**, 129.

area, but none over the pressure range investigated by Burrage. The essential shape remains unaltered after the most drastic flushing out treatment, and even after evacuating the gel at 800°C .

I. Experiments by Static Vacuum Method.

The static vacuum technique employed was identical with that described by Burrage,¹ and subsequently used by the author,⁴ for the deter-

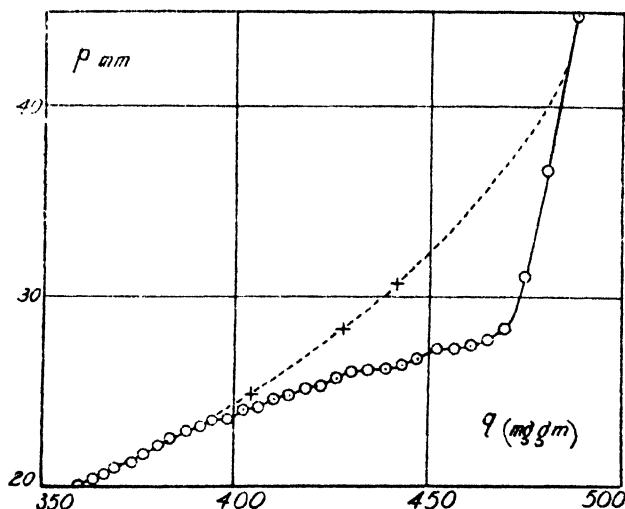


FIG. 1.— CCl_4 on Silica Gel B. Hysteresis Loop.

mination of isothermals of the alcohols on silica gels, one of which, "gel B," has been used in the first series of the present experiments. A sample weighing about 5 gms. was evacuated at 150°C ., and a few sorption points were determined by direct weighing, after charging to a known pressure with carbon tetrachloride vapour. The desorption curve was then investigated in detail by the "pressure change" method. From $q = 498$ mg. gm. to $q = 360$ mg. gm. a total of 34 points was determined, with an average separation of 3.5 mg. gm. The upper part of the curve, shown in Fig. 1, revealed a few definite breaks, but the lower portion showed none, although a few of the points were irregular. The gel was then heated to about 100°C ., with a moderate pressure of carbon tetrachloride vapour, for several hours, but after evacuation and recharging, the isothermal remained unaltered by this "flushing out" treatment.

A second experiment was carried out a year later, using a fresh sample of gel which was flushed out twice at 80°C ., and evacuated at 150°C before determining the isothermal. This showed two very definite breaks

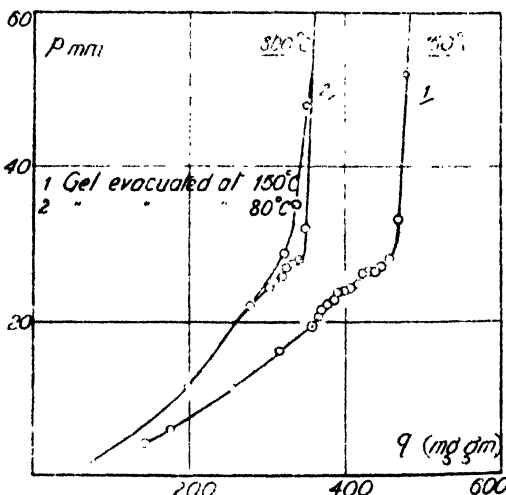


FIG. 2.— CCl_4 on Silica Gel B.

in the high pressure region, Fig. 2,—one at 26.2 mm., where three points

were obtained between $q = 438$ and $q = 421$; and another at 23.6 mm., which was less sharply defined. The original experiment, Fig. 1, gave breaks at 27.2, 26.2 and 23.6 mm. Further examination of the isothermal down to a pressure of 4 mm., gave no indication of any discontinuities although 100 points were determined. The gel, containing about 140 mg. gm. of adsorbed carbon tetrachloride, was then heated for several hours at 120° C., evacuated and recharged. The isothermal was then examined in detail from 17 mm. down to 1.8 mm. and showed a number of rather irregular discontinuities. A portion of this curve is shown in Fig. 3. The sudden fall in pressure from 2.24 mm. to 2.0 occurred after the gel had been left overnight. The longest break is about 4 mg. gm., which is less than the average values found by Burrage.

The gel, which now contained 76 mg. gm. of adsorbed carbon tetrachloride, was heated to 250° C. A considerable pressure was generated, sufficient to blow out the barrel of the container tap, indicating that a reaction was taking place between the adsorbed vapour and the residual water of the gel. The treatment was continued for 12 hours and the gel then evacuated at 150° C. before the third run was begun. This desorption curve showed breaks at 27.1 mm., and 26.1 mm., but at lower pressures the discontinuities were no more definite than before. The gel was flushed

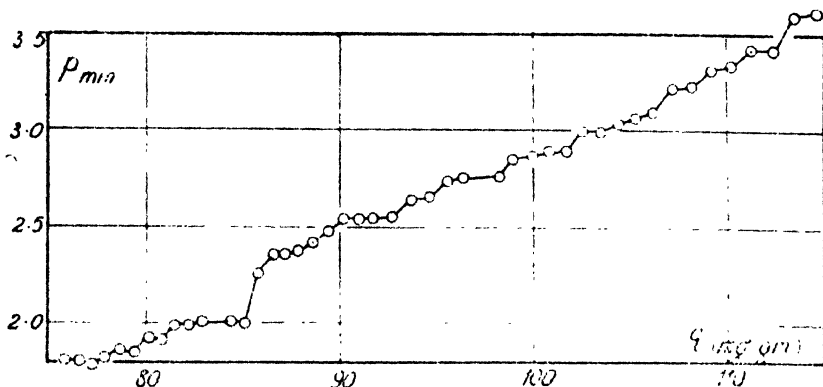


Fig. 3.— CCl_4 on Silica Gel B.

out again, evacuated at 400° C., and a fourth isothermal determined, which showed breaks at 27.3 and 26.7 mm. The "ascending" branch of the hysteresis loop was also examined this time.

Finally, the gel was evacuated for a few hours at a temperature of 800° C. and a fifth curve determined. This is shown in Fig. 2, curve 2, and although the isothermal has shifted back towards the pressure axis and falls more steeply, there is no fundamental difference in shape, and the hysteresis phenomena still persist. The final evacuation of the gel showed that the zero weight had diminished by 5.4 per cent., and the data for this isothermal have been calculated from the final weight of the gel, taking into account this loss of water during flushing out and evacuation.

The second series of experiments was carried out with a sample of gel from the batch used in the work of Allmand and Burrage,² and on which the step-like discontinuities were subsequently found by Burrage.² An isothermal was first determined on a sample of gel weighing about 2 gms., evacuated at 110° C., the temperature used by Burrage. This gave the isothermal shown in Fig. 4, curve 1, which although irregular, shows no definite breaks, and is similar to that determined by Allmand and Burrage.² The gel, containing about 100 mg. gm. adsorbed vapour, was heated to 60° C. for 8 hours, evacuated and recharged. An examination of the isothermal between 3.2 and 2.5 mm. gave no very definite breaks. The

gel was then heated to 100° C. for three hours, also without effect. A third "flushing out" treatment, at 120° C. for 3 hours, also failed to reveal any discontinuities and the position of the isothermal remained unaltered. A repetition of this treatment, however, produced a remarkable change in the shape of the isothermal, the result being shown in Fig. 4, curve 2. The pressure fell from 8.9 mm. at $q = 217$ to 0.4 mm. at $q = 201$. Below this concentration the pressures were too small to measure accurately on the mercury manometer. The gel was charged again to a higher pressure and a second desorption curve obtained which was almost identical with the first. The gel, containing about 200 mg. gm. of carbon tetrachloride (at a pressure of 1 mm. at 25° C.) was heated to 150° C. for 1 hour. A considerable amount of the adsorbed vapour condensed out on the cooler portion of the gel container, near the tap and was pumped away before raising the temperature to 250° C. At this temperature a pressure greater than one atmosphere was generated inside the container and the tap was again blown out. The temperature was raised to 400° C. after further

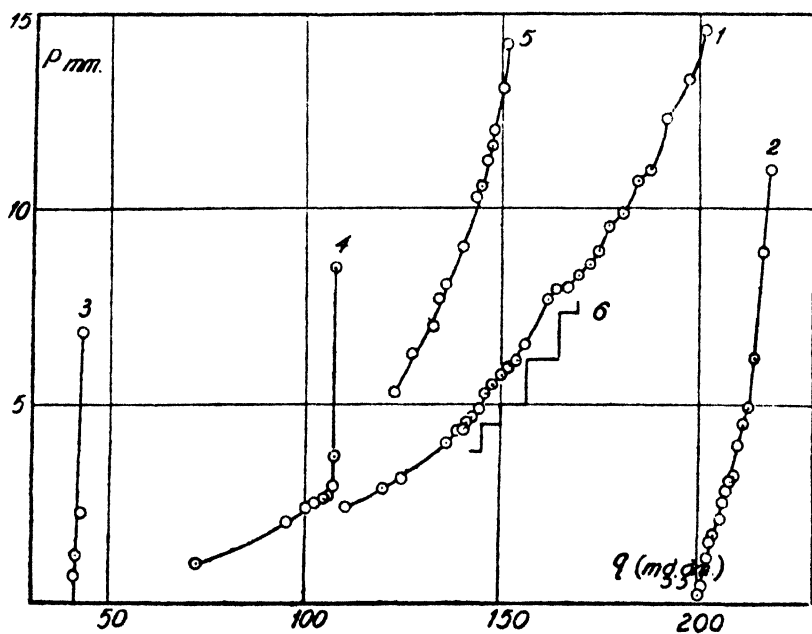


FIG. 4.— CCl_4 on Silica Gel A.

evacuation, but a pressure was still developing inside the container, presumably due to the reaction between carbon tetrachloride and the structural water of the gel, since fumes of hydrogen chloride were observed. This drastic treatment caused a considerable decrease in the adsorptive power of the gel, the final isothermal, Fig. 4, curve 3, rising almost vertically towards saturation between 40 and 45 mg. gm.

Another experiment was carried out using a larger amount of gel, about 6 gms., which was evacuated at 110° C. and flushed out at 60° C. for 4 hours. An examination of the isothermal between 4.0 mm. and 2.5 mm. gave a curve which, although discontinuous, was also exceedingly irregular. The gel was next flushed out at about 110° C. and a second isothermal determined which is shown in Fig. 4, curve 4. The discontinuities were less irregular than before, but no definite breaks were found. The top portion of the isothermal is of interest as it appears to represent a stage intermediate between curves 2 and 3 although the middle part still resembles curve 1.

A final experiment with another portion of the gel was performed in order to study the effect of heat treatment alone, without any "flushing out" treatment. 5 gms., evacuated at 150°C ., decreased in weight by 3 per cent. after evacuation at 400°C . The isothermal shown in Fig. 4, curve 5, has no very definite breaks.

At one point the gel was heated to 70°C . for four hours before resuming the pressure measurements at 25°C ., but no increase in pressure occurred. After the last point had been determined, at 5.34 mm. pressure, the container was heated to 120°C . for 2 hours and then opened to the manometer after reducing the temperature to 25°C . The pressure had risen to nearly 15 mm. On opening the dead space to a freezing bulb immersed in liquid air, the pressure fell to zero, but with the freezer at -126°C . (immersed in melting methyl cyclohexane) a pressure of 1.3 mm. was recorded; which may denote the presence of either CO_2 or HCl . After a final evacuation at 150°C . the gel retained 8.4 mg. gm. of carbon tetrachloride.

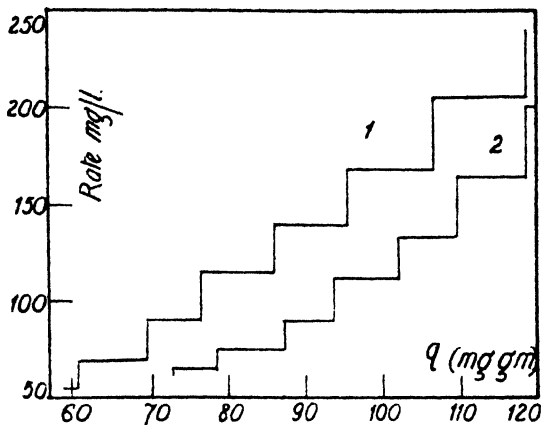


FIG. 5.—Carbon tetrachloride on Silica Gel.
Retentivity method.

Discussion.

The isothermals of carbon tetrachloride on "gel B" are similar in shape to those of the aliphatic alcohols⁵ except at low pressures. The amounts of methyl and butyl alcohol taken up at saturation are 300 and 290 mg./gm. respectively, corresponding to 0.380 and 0.370 c.c./gm. The figures for carbon tetrachloride are 528 mg./gm., or 0.330 c.c./gm. The hysteresis loop extends over a range of about 0.056 c.c./gm. which is greater than the highest value found for the alcohols, 0.038 c.c./gm. It is interesting to note that with ethyl alcohol⁴ and isopropyl alcohol,⁵ discontinuities were also observed in the descending branch of the hysteresis loop. With carbon tetrachloride, the main break occurs at 26.2 mm., which corresponds to a capillary radius of 13.4 Å., calculated according to the Kelvin equation. The values calculated from the alcohol isothermals lay between 14 and 16 Å.

It has previously been shown by the author that the hysteresis phenomena observed with ethyl alcohol on this gel remains unaltered even after the most drastic flushing out treatment and after evacuation at 350°C . instead of the usual temperature of 150°C . The present series of experiments with carbon tetrachloride on the same gel confirms this result and it has now been shown that the hysteresis phenomena persist even after evacuating the gel at 800°C .

In the low pressure region the isothermals of carbon tetrachloride differ considerably from those of the alcohols. At a relative pressure of 0.01, the gel takes up 92 mg./gm. of methyl and 177 mg./gm. of butyl

⁵ Foster, *Proc. Roy. Soc., A*, 1935, **150**, 77.

alcohol; these amounts correspond to 0.0028 and 0.0024 gm. mol./gm. respectively. At the same relative pressure only 70 mg./gm. of carbon tetrachloride are held, which represents 0.0004 gm. mol. or only one-sixth the number of molecules.

The other sample of silica gel gives irregular isothermals before it is subjected to any flushing out treatment, and the isothermal shown in Fig. 4, curve 1, is similar to that determined some years previously by Allmand and Burrage² under similar conditions. In the present investigation mild flushing out treatment as employed by Burrage¹ has little effect either upon the position or the shape of the isothermal, but the final result of drastic flushing out treatment is remarkable, giving the isothermal shown in Fig. 4, curve 2. The step-like breaks observed by Burrage, also shown in this diagram, curve 6, appear to represent some intermediate stage in the transition, whilst the final curve resembles the isothermals determined by McBain⁶ on highly purified sugar charcoals, which are regarded by him as the "ideal type," to which all isothermals should approximate when impurities are eliminated. At a relative pressure of 0.01 the gel initially takes up about 70 mg. gm. or 0.0004 gm. mol, and is saturated at about 200 mg. gm. After the drastic flushing out treatment, which does not cause any increase in the saturation volume, 200 mg. gm. or 0.0013 gm. mol is held at a relative pressure lower than 0.01, so that the actual amount of carbon tetrachloride so held has increased threefold, and represents 76 per cent. of the total sorption. Comparing the pressures developed when 200 mg. gm. are adsorbed, it is found that the initial pressure of 10 mm. before flushing out, fall to 0.2 mm.—corresponding to an increase in the adsorption potential from 800 cal. to 4000 cal./mol.

The isothermal of ethyl alcohol on the gel used in these experiments is similar to that described on "gel A," one of the two samples previously examined by the author, and shows that at a relative pressure of 0.01 the gel takes up 104 mg. gm. or 0.0023 gm. mols. This represents 60 per cent. of the total sorption so that the isothermal already approximates to the ideal type. It is further important to note that these alcohol isothermals do not alter in shape after drastic flushing out treatment.⁴

Previous work on ferric oxide gel⁷ indicated that the formation of the unimolecular layer was practically complete at a relative pressure of 0.01 and a rough estimate of the surface area of the gel was made by assuming that the alcohol molecules occupied an area of 20.5 Å² each. This is a minimum value which will only be attained if the adsorbed molecules are oriented with the hydrocarbon chain normal to the surface. A similar calculation from the above data for ethyl alcohol on silica gel gives the value 2.86×10^6 cm.² for the surface per gram.

It is reasonable to suppose that the 200 mg. gm. of carbon tetrachloride, which is so firmly held after the flushing out treatment, also represents a close-packed unimolecular layer. The diameter of the adsorbed molecule is almost exactly 6 Å and on account of its symmetrical nature it is unnecessary to make any assumptions as to its orientation. If the sectional area be taken as 36 Å² the surface area of the gel per gram is found to be 2.84×10^6 cm.²—a value identical with that calculated from the alcohol isothermal.

⁶ McBain, *Sorption of Gases and Vapours by Solids*.

⁷ Foster, *Proc. Roy. Soc., A*, 1934, 147, 128.

This shows that the carbon tetrachloride, which is strongly adsorbed on the flushed out gel, covers approximately the same surface area as is occupied by ethyl alcohol on the untreated gel, and since there is no change in the total adsorptive capacity, it appears that the only result of flushing out has been to alter the nature of the surface on which the sorption process occurs.

The residual water content of silica gels after evacuation at about 200° C. is of the order 5 per cent.; the removal of more water causes a decrease in activity, and the last traces can be removed only by prolonged treating at about 1000° C., which breaks down the gel structure. Little is known of the manner in which this residual water is held,* but the vapour pressure at 200° C. is less than 10^{-4} mm. Hg. during the final stages of evacuation, and there is no evidence that this water can be displaced by other adsorbed substances at ordinary temperatures. During the flushing out treatment, however, some water must evidently react with carbon tetrachloride.

After the removal of this residual water, together with the products of hydrolysis, carbon tetrachloride is able to become more firmly attached to the gel surface. It is important to note that removal of water by heat treatment alone, in vacuum, does not suffice. This is illustrated by Fig. 4, curve 5, which shows the isothermal obtained with a sample of gel initially evacuated at 150° C., then further evacuated at 400° C. The gel had then lost 3 per cent. or 30 mg./gm. of water, but subsequently failed to show any increase in the amount of carbon tetrachloride taken up at low pressures. A rough calculation shows that the area occupied by the removed water is able to accommodate at least 70 mg./gm. of carbon tetrachloride.

The essential change in the surface must therefore occur during the chemical reaction between adsorbed water and carbon tetrachloride. The process cannot be regarded as an "activated" adsorption, taking place when the temperature is raised, because the "flushing out" is performed when comparatively little carbon tetrachloride is present; the main bulk is added later at room temperature, after further evacuation, and is then strongly adsorbed. Fig. 4, curve 6, shows that removal of still more water from the gel, by further heating with adsorbed carbon tetrachloride, results in greatly diminished activity, although the isothermal retains its characteristic shape.

II. Experiments by the Dynamic Retentivity Method.

An extensive series of experiments was carried out using the improved air-stream technique described by Burrage.³ Most of the systems investigated have now been examined by the more accurate static vacuum method, and the few examples given below will serve to illustrate the unreliability of the retentivity method.

i. Carbon Tetrachloride on Silica Gel.

The retentivity method gave very definite breaks similar to those described by Burrage.³ Fig. 5, curve 1, represents the results obtained with about 3 gms. of gel and an air stream of 400 c.c./min. Curve 2 was

* The residual water must be held partly on the surface and partly "locked up" in the interior of the gel. The latter may be present as silicic acid complexes whilst the former may exist in the form of hydroxyl groups attached to the silica atoms of the SiO_2 lattice, as suggested by Rideal (*Trans. Faraday Soc.*, 1936, **32**, 4).

obtained on the same sample three weeks later using a 200 c.c./min. rate. Although there is a horizontal shift away from the p. axis of about 10

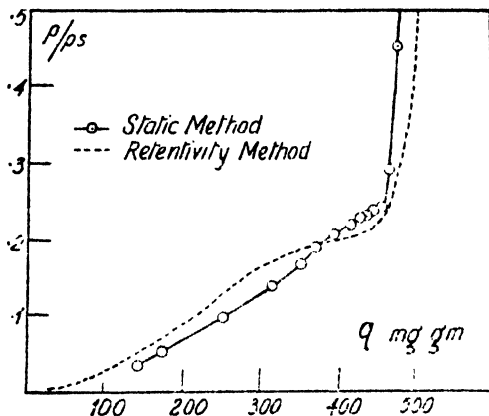


FIG. 6.—Carbon tetrachloride on Silica Gels.

mg./gm., the steps occur at very nearly the same pressures as before. The gel used here was a sample from the same batch as "Gel A," previously described by the author⁴ and has similar characteristics to that used by Burrage.

Isothermals were also determined on another sample, "Gel B," also described previously.⁴ In Fig. 6 the curve obtained by the static vacuum method is compared with the smoothed out retentivity curve (drawn through the middle point of all steps where present). The latter

is evidently only a rough approximation to the true isothermal.

ii. Ethyl Alcohol on Silica Gel.

An account of an investigation of this system by the static vacuum method has already been published.⁴ Below about 5 mm. pressure the retentivity method gave remarkable curves showing a regular step-like structure similar to the carbon tetrachloride isothermals. Two samples of gel were investigated and the pressures at which the breaks occurred were in many cases identical—Fig. 7. The average length of the steps is 2.5 mg./gm., but in both investigations by the static method, points were obtained less than 0.5 mg. apart, without any signs of horizontal breaks, even after drastic flushing out treatment, including refluxing the gel with ethyl alcohol for several hours before evacuation.

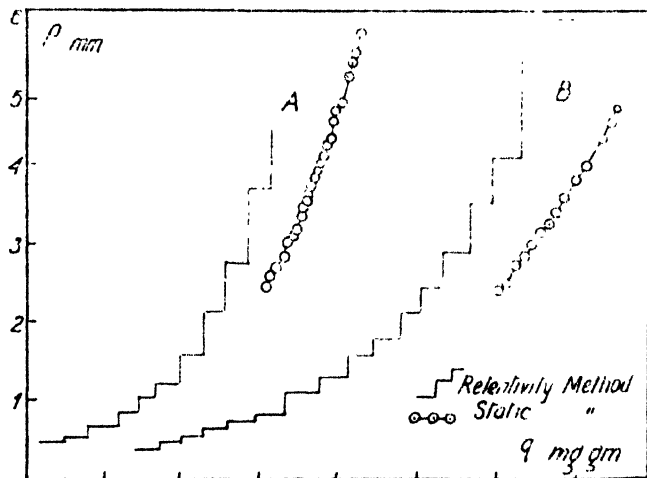


Fig. 7.—Ethyl alcohol on Silica Gels.

Fig. 8 shows the complete isothermals obtained by the different methods. The curves for "gel B" coincide over the first 20 mg./gm. of the desorption process, after which the static curve falls more rapidly. With "gel A" the agreement is better, showing that when applied to isothermals of normal type, the dynamic method gives a fair approximation to the true isothermal, whereas with isothermals of abnormal type the results obtained over the middle range of the sorption process are in error.

iii. Water on Silica Gel.

This system provides the most striking example of the failure of the dynamic retentivity method. The extensive examination of water isothermals on silica gel at 60° C. and 70° C. carried out by Lambert and Foster⁸ using a static vacuum method, failed to reveal any discontinuities, although horizontal breaks had been reported by Allmand and Burrage⁹ using the retentivity method at 25° C. The sorption of water by two samples of silica gel has now been examined in detail by both methods at 25° C. Fig. 9 shows the results obtained with "gel A." The retentivity curve is similar to that described by Allmand and Burrage, whilst the static curve resembles those obtained by Lambert and Foster. On gel B, the two curves follow one another closely from saturation down to $q = 180$, after which the retentivity curve is distorted, Fig. 10. Here the static method shows that between $q = 210$ and 280 the pressure changes only from 8.0 to 8.3 mm., but there is no evidence of any abrupt pressure changes.

Discussion.

The results obtained with ethyl alcohol on silica gel "A" (Fig. 8) show that when the isothermal is of normal type, the pressure falling steeply with concentration until quite low values are reached, the retentivity method gives a fair approximation to the true isothermal determined by the static vacuum technique. The latter, however, gives no indication of any step-like discontinuities.

The data for the other systems, which give abnormal isothermals, in which the pressure falls slowly over

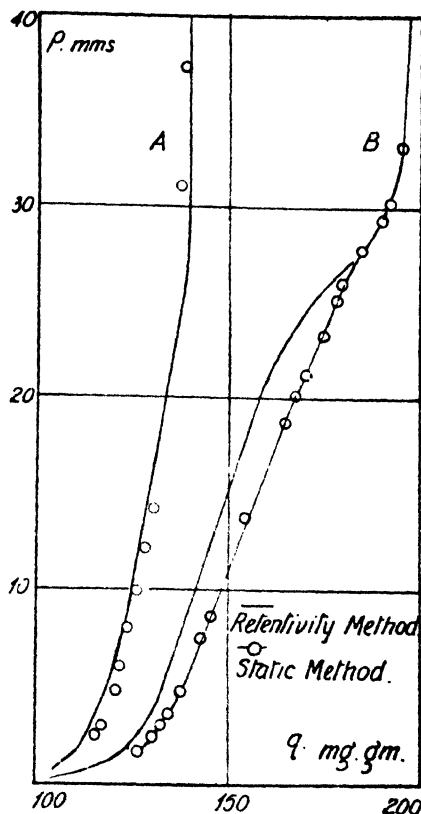


FIG. 8.—Ethyl alcohol on Silica Gels.

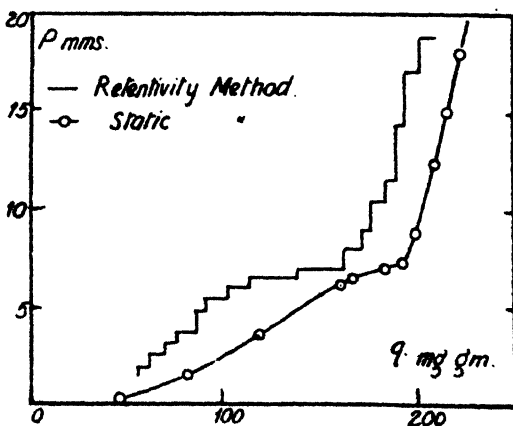


FIG. 9.—Water on Silica Gel A.

⁸ Lambert and Foster, *Proc. Roy. Soc., A*, 1931, 134, 246.

⁹ Burrage, *J. Physic. Chem.*, 1930, 34, 2202.

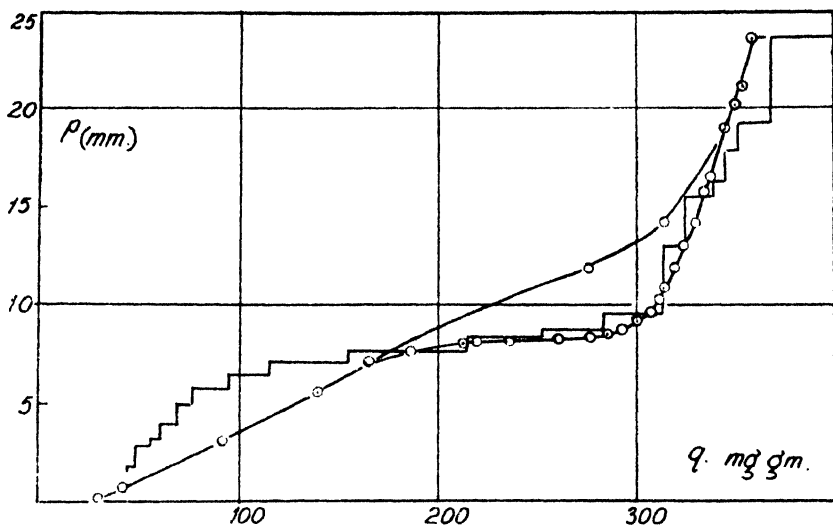


FIG. 10.—Water on Silica Gel B.

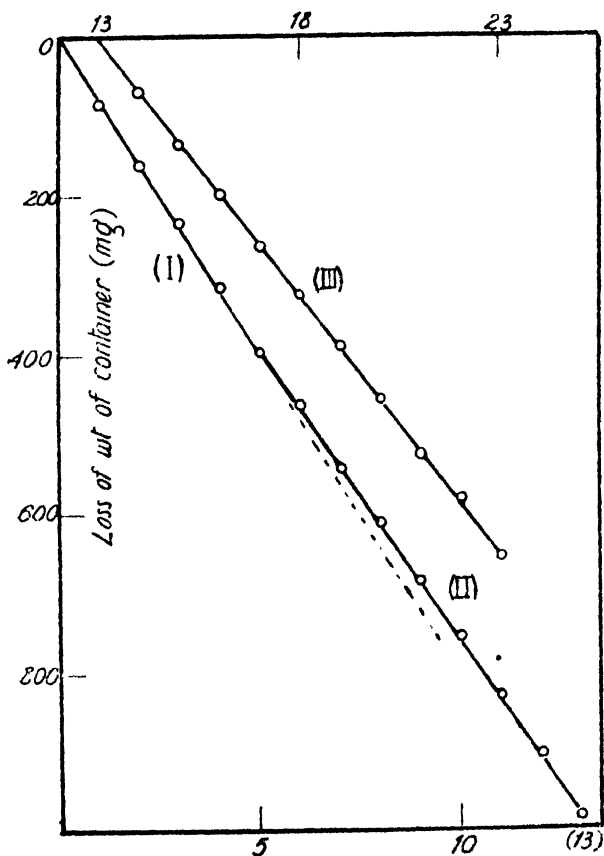


FIG. 11.

the middle concentration range, show that the retentivity method breaks down. The agreement is reasonably good at the beginning of the desorption process, but after the middle of the flat portion of the isothermal has been reached, the pressures on the retentivity curve remain higher than those at corresponding points on the true isothermal, whilst the final drop in pressure occurs at a lower concentration and is more abrupt. The derived isothermal thus suffers a maximum distortion in the middle concentration range, which makes it impossible to apply any simple correction to obtain the true curve—such as that suggested in the modified retentivity technique.³

A typical retentivity curve, obtained by plotting the weight of charged gel against the amount of air passed, is shown in Fig. 11. This appears to consist quite definitely of a series of linear portions of gradually diminishing slope, corresponding to horizontal breaks in the pressure concentration curve, since the rate of loss dq/dv is assumed to be proportional to the pressure. A close examination of the actual loss of weight between consecutive readings shows very large variations from the mean value.

Curve.	Loss of Weight. (mg./gm.).	Mean Value.	Maximum Deviation from Mean.
I.	82, 78, 74, 80, 84	79.6	+ 4.4 to - 5.6
II.	68, 78, 68, 70, 66, 74, 76, 78	73	+ 5 to - 7
III.	66, 66, 66, 66, 62, 64, 68, 68, 56, 74	65.6	+ 8.4 to - 9.6

It is evident that a method which gives results of this nature cannot follow small changes of pressure with any degree of accuracy and probably merely shows the average value of the pressure over a fairly wide concentration range.

Summary.

I. Isothermals of carbon tetrachloride on two samples of silica gel have been determined at 25° C., using a static vacuum method.

II. The effect of heat treatment and flushing out has been examined, but no well-defined discontinuities have been observed under any conditions.

III. After prolonged heating at 120° C. with carbon tetrachloride, some of the residual water is removed from the gel, and a marked alteration occurs in the shape of the isothermal, resulting in greatly increased adsorption at low pressures.

IV. The dynamic retentivity method has been used to determine isothermals of water, ethyl alcohol and carbon tetrachloride on silica gel. A comparison of the results with those obtained by the static technique shows that the retentivity method is quite unreliable when applied to isothermals of abnormal type.

The author wishes to acknowledge the receipt of a Senior Award from the Department of Scientific and Industrial Research whilst some of this work was in progress.

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ON THE STABILITY OF ABIARANA GUTTA-PERCHA LATEX.

BY F. K. DANIEL, H. FREUNDLICH AND K. SÖLLNER.

Received 7th August, 1936.

I.

Although it has long been known that the rubber latices of different species of trees differ widely as to their stability, very little information can be found in the literature.¹

We compared the properties, mainly the stability, of an Abiarana Gutta-Percha latex (*Lucuma lastiocarpa*, Family Sapotaceae, Tribe *Mimusops*) with those of the fairly well-known *Hevea brasiliensis* latex. (The *Hevea* latex we used was an ammonia preserved latex of about 35 per cent. dry rubber content.) As we had only a very small sample of about 40 c.c. of the Abiarana latex, a second small sample of the same appearance and the same properties, the origin of which was not ascertained, was also used. We have good reasons to believe that it also was an Abiarana Gutta-Percha latex. For both samples and the analysis we are greatly indebted to Mr. W. H. Stevens,² London.

TABLE I.—ANALYSIS OF SAMPLE OF ABIARANA GUTTA-PERCHA LATEX.

	Per Cent. on the Latex.
Total solids	37.1
Crepe (by acetone, washed on rolls and dried)	33.6
Whence total solids excess	3.5
Diffusate (70 hours) by direct measurement	3.4
Specific gravity	0.984
Acetone extract of dry crepe	2.2
Nitrogen content of dry crepe	0.20
Gutta hydrocarbon (by difference)	31.2
Distribution of the Nitrogen:—	
	Per Cent. on Latex. Per Cent. on Dry Material.
Total solids	0.33 0.89
Crepe	0.20 0.59
Diffusate	0.17 4.97

According to Mr. Stevens' information neither of the samples contained preservatives. Both had, when we got them, a p_H of about 5.3 and a strong smell of fermentation. They remained stable and unchanged in every respect during the many months we had them under observation. *Hevea* latex, on the other hand, coagulates within a few hours unless preservatives such as ammonia are added.

In the course of some days the Abiarana latex always creamed up, forming a very concentrated cream of about 80 per cent. above an opaque,

¹ Cf. for instance E. A. Hauser, *Latex*, Dresden and Leipzig, 1927.

² W. H. Stevens, *India Rubber J.*, 1935, 90, 36.

yellowish serum. On being shaken the cream disperses again completely and under the microscope only single particles in vivid Brownian movement are observed. They are perfect spheres of 1.2μ diameter.

The behaviour of the two latices towards electrolytes is even more markedly different. Hevea latex coagulates readily, forming one single lump of rubber above a clear serum; if the latex is very dilute, the rubber forms coherent strings which curdle at once on slight agitation. Abiarana latex on the other hand cannot be coagulated irreversibly by electrolytes; if they are added, the Abiarana creams up rapidly; on shaking the cream readily redisperses; thereafter creaming-up, (which takes just as long as before) and redispersion can be repeated at will.

The cause of the different behaviour of the two latices is recognized by microscopic observation; in a solution of $p_H > 6$ both have almost exclusively single particles, and although occasionally two or more approach or even collide, they do not cohere, but either repel one another immediately or rapidly rotate together for some seconds and then suddenly separate again.

In a solution of a p_H of about 3.5 to 5, or in a solution of a $p_H > 6$ with a suitable amount of salt, a difference becomes apparent. With the Hevea a certain fraction of the collisions leads to irreversible aggregation, *i.e.*, the particles do not separate again; their joint Brownian movement is smaller and their creaming velocity higher. On creaming-up they collide with other particles or aggregates and thus grow larger and larger in course of time. If, however, very few particles are in the liquid (*e.g.*, in 1:5000 dilution), the number of collisions may be so small that a cream is formed containing not too large aggregates. These can be dispersed in the liquid by careful agitation, but, by shaking strongly, they unite to one single lump of rubber. Hence a sharp strong movement of the liquid can produce an even stronger effect than the Brownian movement, so that the total number of collisions depends on the concentration of the latex and on the movement of the liquid. The percentage of irreversible collisions depends on the degree of discharge of the particles caused by the addition of acid or salt. It increases with increasing discharge. Thus the velocity of coagulation depends on, at least, two factors: concentration of the latex and state of discharge. If the particles are so weakly discharged that coagulation is a slow process, it may be accelerated by shaking vigorously, because this greatly increases the total number of collisions and hence the fraction of irreversible collisions too.

The Abiarana particles also, when acid or salt is added, form aggregates, depending on the concentration of the latex and the degree of discharge. The more concentrated and the more discharged, the more and the larger aggregates are formed, and, therefore, the higher is the creaming velocity. But these aggregates, or nearly all of them, are reversible, and either break up spontaneously or are dispersed by sharp agitation of the liquid, by collisions with other particles or aggregates, or by an impact with the wall. They, therefore, do not grow indefinitely in course of time, as is the case with Hevea; an equilibrium is established between association and dissociation. One fraction of collisions causes the breaking up of aggregates which have been produced by another fraction. The ratio of these two fractions determines the size and number of the aggregates. Such equilibrium conditions continue when the latex is shaken, and the redispersion of the aggregates seems to take place even more quickly than their formation, in contrast to the behaviour of the Hevea latex.

The parallelism between state of discharge, aggregation and creaming velocity is very obvious (*cf.* Table II.). A given p_H and latex concentration always involve a given distribution of the particles: a corresponding fraction of them unites to aggregates of characteristic sizes, the fraction of single particles also being characteristic.

The aggregates of Abiarana are much smaller than those of Hevea, even when the latter are observed immediately after being discharged,

TABLE II.—PARALLELISM OF DEGREE OF DISCHARGE, AGGREGATION AND CREAMING VELOCITY OF AN ABIARANA LATEX (1 : 100 DILUTED).

Acetic Acid (in Millimol).	Creaming Velocity.**	State of the Particles (Determined under the Microscope).
—	> 48 ^A	95 per cent. of the units * are single particles. 5 per cent. are present as aggregates. Most of them contain 2, and in a few cases 3, particles.
1.00	36 ^A	About 50-70 per cent. of the units are single particles. Many aggregates contain 2 and 3 particles. Few bigger aggregates are present.
1.25	4 ^A 30'	About 30-50 per cent. of the units are single particles. Many aggregates contain up to 12 particles, but most of them only 2-5.
1.43	3 ^A 20'	Only few units are present as single particles. Aggregates are formed up to 20 particles, and some even larger. Most of them, however, contain 3-9 particles.

* Each aggregate, irrespective of its size, is counted as one unit, because otherwise the percentage of single particles would be very difficult to estimate.

** The latex was discharged to a different degree by adding different amounts of acetic acid. Creaming velocity was determined as follows: the latex containing the acid was filled into normal test-tubes to a height of 2 cm. and the time was noted when the latex particles had creamed up so far that the lower 1 cm. of the liquid had become so transparent that print could be read through it. The time for complete creaming up was less characteristic because with decreasing concentration of particles the number of collisions also decreases, so that a certain percentage of unaggregated or poorly aggregated particles remains, the creaming velocity of which is small and ill-defined.

The second and third column of Table II. do not seem to agree so strictly as expected. The comparatively high percentage of single particles observed under the microscope is partly due to the difference in experimental conditions. The number of collisions which can occur in the 1 mm. cavity of the slides, is much smaller than in a layer 2 cms. high. Once the particles have come close to the cover glass they are checked in their free movement and are rarely able to aggregate. The aggregates already formed, however, collide more frequently with the wall than they do in the test tube, and therefore their chance of being broken up is bigger under the microscope than in the test tube. For these two reasons, the number of single particles and the degree of aggregation on the whole must be different under the two conditions; more single particles and less and smaller aggregates will be seen under the microscope.

because in the Abiarana latex the number of collisions resulting in aggregation is much smaller. The particles dispersed by shaking show their old vivid Brownian movement and seem identical in every respect with the original single particles. We assume that the Abiarana particles do not approach each other so closely in the aggregates as do the Hevea particles, owing to strong hydrophilic layers around them though a magnification of 1100 shows no difference in the particle distance of Hevea and Abiarana aggregates; in both the particles retain their original shape.

We shall henceforth call the irreversible aggregation of Hevea latex "coagulation," and the reversible aggregation of Abiarana latex simply "aggregation."

The particles of both Abiarana and Hevea are negatively charged and therefore the aggregation (creaming-up) also of the former mainly depends on the nature of the cations, specially their valency (*cf.* Table III.).

A concentration of mono- and divalent cations larger than that given in Table III. increases the creaming velocity. A considerably larger

TABLE III.*—AGGREGATION VALUES (MILLIMOL/LITRE) OF AN ABIARANA LATEX (1 : 100 DILUTION).

KCl.	BaCl ₂ .	AlCl ₃ .	Th(NO ₃) ₄ .	CuCl ₂ .	Acetic Acid.
100	15	0.66	0.11	2	1

* These measurements were done in a simpler way than those in Table II. We determined the electrolyte concentration which caused the latex, diluted 100-times, to cream up within 2 hours. The test-tubes, containing latex + electrolyte in different concentrations, were stood in a row, and it was easy to fix the critical concentration which could cause a distinct change in the distribution of the particles, in the course of 2 hours, while that just below did not do so. In the experiments of Table III. creaming-up had not proceeded so far as in those of Table II.

concentration of tri- and tetravalent cations and of H⁺-ions diminishes the creaming velocity, because these cations are able to recharge the particles positively and thus to reduce or even to entirely prevent aggregation. The reversal of charge was proved by cataphoretic tests.

II.

What is the cause of the different stability of Abiarana and Hevea latex? The stability of Hevea seems to be mainly determined by proteins. With Scholz³ we are inclined to assume that proteins sensitise the latex and render it rather hydrophobic. Scholz has found on comparing a protein-free Hevea latex with (a) an ordinary latex, and (b) with a protein solution, that the latex behaves as if it were sensitised towards all cations except the monovalent ones.

From the behaviour of the Abiarana latex we conclude that it is most likely a protected hydrophilic system. A strongly adsorbed, hydrophilic layer round the particles prevents them from approaching each other so closely that the attracting forces become predominant. This simple assumption makes the behaviour, described above, perfectly understandable.

It also explains the fact that when migrating under the influence of an electric current, the particles of Hevea form a beautifully coherent skin on the anode, (the phenomenon which renders the "anode process" feasible), while the particles of Abiarana though they are also deposited on the anode to a certain extent, do not ever form a coherent skin, but remain separated from each other and readily redispersable.

The following experiment proves that (as in a normal protected suspension) the Abiarana particles have adsorbed a foreign substance, which is also contained in the serum. If the cream is separated from the serum and shaken up with water, the aggregates are easily redispersed and cream up again readily on adding acetic acid. If this washing process is repeated several times, the latex at last creams up rapidly without addition of acetic acid and is even partly coagulated. The Abiarana latex, then, when deprived of a protecting substance contained in the serum, behaves like Hevea latex, so that the difference in the stability of the two latices must mainly be due to the presence of a protecting substance in the Abiarana and not to other factors as, for instance, the different consistency of the particles.

This experiment proves further that the protecting substance is

* P. Scholz, *Kautschuk*, 1928, 4, 5.

adsorbed reversibly, in a true adsorption equilibrium, a fact being by on means obvious. Consequently precise conclusions concerning the Abiarana latex in normal concentration cannot be drawn from the behaviour of single latex particles in microscopic cataphoretic measurements. For these are carried out in a latex diluted 1000-times or more. This dilution corresponds to a strong washing out. Hence distinctly less of the protecting substance, which normally determines predominantly the properties of the latex, is left adsorbed on the particles. Kemp and Twiss⁴ have drawn the same conclusions from the results of cataphoretic measurements with Hevea latex.

Another proof of the protecting action of the reversibly adsorbed substance is the fact that the washed Abiarana latex coagulates readily on being boiled, whereas unwashed Abiarana, treated in the same way, remains stable.

That the protecting substance is actually contained in the serum can easily be shown by the fact that if a sufficient amount of Abiarana serum is added to Hevea latex, the mixture is stable like the Abiarana latex itself; on adding acetic acid it does not coagulate, but only aggregates and creams up. A mixture of the whole Abiarana latex plus Hevea latex behaves of course in the same way.²

A rough quantitative investigation shows that one part of Abiarana latex completely protects one part of Hevea, if both are in their original concentration (about 35 per cent.). If diluted, less Abiarana is required e.g., one part of Abiarana diluted 1 : 50 protects three parts of Hevea of the same concentration.

A mixture of Hevea latex with a sufficient amount of Abiarana latex or serum is, like pure Abiarana, stable on being boiled, unless it has been washed beforehand. On being washed, as described above, the mixture behaves similarly to Abiarana latex, the only difference being that less washing is necessary to remove so much protecting substance as to effect coagulation. After washing, the mixture coagulates in just the same way as does pure Hevea.

III.

We tried to find out the chemical nature of the protecting substance contained in Abiarana latex.

Since the charge of its particles can easily be reversed by H⁺ -ions, even after the latex has been dialysed, one could assume an ampholytic substance of the protein type to be the responsible factor. It should, it is true, be a protein, which is much more hydrophilic than the protein which determines the behaviour of Hevea latex.

The products of splitting proteins are usually more hydrophilic than the proteins themselves. Hence we investigated the reactions of Abiarana latex towards several specific reagents for proteins and the products of splitting them. In Table IV. the behaviour of Abiarana, Hevea and peptone (BDH products) are compared.

The table reveals a marked resemblance of the reactions of Abiarana with those of peptone. Several other protein products also, not mentioned in the table, such as lysalbinic acid, etc., show similar reactions. We therefore tested, whether Hevea latex could be stabilised by protein products, as it is by Abiarana serum. No protecting action was observed, with protalbinic acid, lysalbinic acid, peptone, or with any of the many

⁴ I. Kemp and D. F. Twiss, *Trans. Faraday Soc.*, 1936, **32**, 890.

TABLE IV.—BEHAVIOUR OF HEVEA, ABIARANA AND PEPTONE TOWARDS REAGENTS FOR PROTEIN AND THE PRODUCTS OF SPLITTING PROTEIN.

Reagent.	Hevea.	Abiarana.	Peptone.
Acetic acid.	Coagulation.	Microsc. aggregation.	No precipitate.
Formaldehyde.	Coagulation.	Microsc. aggregation.	No precipitate.
Sulphosalicylic acid.	Coagulation.	Stronger microsc. aggregation.	No precipitate.
Trichloroacetic acid.	Coagulation.	Small macrosc. aggregation.	Slight precipitate.
Phosphotungstic acid.	— *	Slight sediment	Slight precipitate.
Biuret test.	Violet-blue.	Blue, coagulation.	Violet-blue.

* Reaction only takes place in neutral or acid solution, in which Hevea is coagulated in any case.

amino acids tested in many different concentrations and after leaving them in contact with the Hevea particles for shorter and longer periods; in all cases Hevea coagulated readily on addition of acetic acid. None of these substances has a stabilising action similar to that of the substance contained in Abiarana, and, therefore, none of them is probably of a similar chemical nature.

Though these experiments are incomplete, we consider it unlikely that any protein disruption products are the cause, for a second reason: On dialysing Abiarana serum through a collodion membrane the substance causing a positive biuret reaction⁵ (see Table IV.) passes through the membrane, whereas the unknown protecting molecules were unable to do so. We could not protect Hevea latex with the liquid outside the membrane, while it was possible to do so with the liquid inside, even after lengthy dialysis. The molecules of the protecting substance are therefore bigger than those of protein products; peptone and lysalbumin acid both pass through the membrane.

The protecting substance in Abiarana latex is probably also not a true protein, because the reactions of Abiarana for proteins are negative and proteins do not so far as has been observed up to now, give a protecting action like that of the Abiarana serum. 9 gm. of gelatin, for instance, per litre of a 3 per cent. Hevea latex does not prevent coagulation. The only difference compared with the coagulation of pure Hevea is, that the system has to be strongly shaken, but this is only due to the high "viscosity" which stops Brownian movement and thus prevents the collision of the particles.

The same applies to other hydrophilic substances, *e.g.*, starch. The coagulation of a 3 per cent. Hevea latex with 9 gm. starch per litre appears to be the same as without it.

Hence we must assume the unknown protecting substance to be of a nature distinctly different from that of the usual protecting agents.

IV.

The results and conclusions of this investigation agree to some extent with those of Moyer who investigated many latices of the *Euphorbia*

⁵ Since our Abiarana latex was several months old when we got it, we are unable to decide, whether the protein degradation products found were present initially or were decomposed from proteins by later fermentation.

species. Applying the Mudd technique of the moving interface, he determined the wettability of the particles⁶ and concluded that the particles of some latices have hydrophilic, those of others more hydrophobic surfaces. Being interested in the latices chiefly from a botanical point of view, he has so far not correlated the observed surface phenomena with the stability of the latices. But Moyer's direct experimental evidence of the widely differing surface properties, though obtained for latices different from Abiarana, enhances the probability of our assumption that the great stability of the Abiarana latex results from the very hydrophilic properties of its protecting agent.

Moyer also determined with 21 species of *Euphorbia* the cataphoretic mobilities, as depending on the p_H , and thus the isoelectric point of their particles.⁷ From a comparison of these curves he concludes that some latices behave as though these particles were completely coated by proteins, others as though protected by a mixture of several proteins or by a mixture of proteins with other ampholytes. A third group of latices is found to behave as though the particles were coated by non-proteins. In spite of the fact that we do not consider (for the reason mentioned above) the cataphoretic method to be quite correct for systems protected by reversibly adsorbed substances, we believe Moyer's results to hold qualitatively. Hence we can take it from him that other stable latices protected by non-protein substances exist.

Summary.

1. The latex of Abiarana Gutta-Percha is more stable than that of Hevea. In the absence of preservatives Abiarana latex is stable for many months, whilst Hevea coagulates readily in a few hours. On addition of electrolytes Abiarana only creams up and is readily and reversibly redispersed, Hevea is coagulated irreversibly. Under the influence of the electric current Abiarana does not form a coherent skin on the anode, Hevea does so easily.

2. The stability of Abiarana latex is due to a protecting substance reversibly adsorbed on the particles. This substance may be removed by allowing the particles to cream-up repeatedly and by separating the serum from the particles.

The serum of Abiarana (or the whole latex) added to Hevea latex strongly protects the latter and causes it to behave like Abiarana latex.

3. A similar protecting action in small concentrations cannot be produced by substances such as gelatin, peptones, lysalbinic acid, starch, etc. The chemical nature of the protecting substance could not be identified. It must have a large molecular weight, since it does not diffuse through membranes.

4. The reversible creaming-up of Abiarana latex is influenced by the cations of the electrolytes added according to their valency, in agreement with the fact that the particles are negatively charged. H^+ -ion and ter- and tetravalent cations are able to reverse the electrical charge of the particles.

5. The difference in creaming velocity due to different electrolyte concentrations (*i.e.*, to different degree of discharge) seems to depend on the average size and number of aggregates of particles which are formed.

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⁶ L. S. Moyer, *Amer. J. Botany*, 1935, **22**, 609.

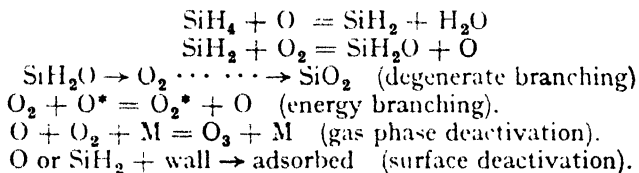
⁷ L. S. Moyer, *ibid.*, 1934, **21**, 293.

EFFECT OF LIGHT ON THE IGNITION OF MONOSILANE-OXYGEN MIXTURES.

BY H. J. EMELÉUS AND K. STEWART.

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The authors have shown¹ that in the thermal oxidation of mono-, di-, and tri-silane ignition occurs when the total pressure of the gas mixture lies between two limits. The values of these vary with temperature, the diameter of the reaction vessel, and the presence of diluent gases and inhibiting substances in a manner which characterises the reactions as branching chain processes, and in the case of monosilane the following tentative mechanism was put forward:—



The SiH_2 radical and atomic oxygen are considered as starting the chains. If this is correct it should be possible to produce active centres by irradiation with light of a suitable wavelength, and thus to initiate the chains in excess of the normal number started thermally. This should cause silane-oxygen mixtures to explode at pressures outside the normal ignition range. The experiments described in this paper were performed to test this point and also, as a preliminary, to determine the conditions under which monosilane will undergo photochemical decomposition.

Absorption Spectra of the Silicon Hydrides.

The absorption spectra of the silicon hydrides were first examined, as no data were available. The three hydrides were prepared in a state of purity by the method of Stock and Somiesky² and stored in glass reservoirs fitted with mercury valves. Photographs were taken on a Hilger small quartz spectrograph (Ilford Q plates; copper arc reference spectrum). The light source was a water-cooled hydrogen discharge tube, operated by a 5000 v. transformer, and taking a current of 0.2 amp. A plane-ended quartz absorption cell, 10 cm. long, was employed.

Monosilane at pressures up to 75 mm. proved to be completely transparent to ultra-violet light down to approximately 1850 Å., the limit of the quartz spectrograph. Disilane and trisilane both absorbed light at wavelengths greater than 1850 Å. The limits of transmission in the 10 cm. cell with varying gas pressures are tabulated below:—

¹ Emeléus and Stewart, *J.C.S.*, 1935, 1182; 1936, 677.

² Stock and Somiesky, *Ber.*, 1916, 49, III.

TABLE I.—LIMITS OF LIGHT ABSORPTION FOR DISILANE AND TRISILANE.

Pressure of Si ₂ H ₆ mm.	12	30	65	—	—	—
Pressure of Si ₃ H ₈ mm.	—	—	—	12	30	60
Limit of Absorption Å.	1980	2000	2020	2140	2170	2190

The absorption in each case was continuous, and in this respect, is similar to that of the simpler paraffins and monogermene.^{3, 4} The absorption limits of disilane and trisilane are higher than that of ethane.⁵

Mercury-Sensitised Decomposition of Monosilane.

The thermal decomposition of monosilane into silicon and hydrogen takes place at 370-500° and has been shown recently by Hogness, Wilson and Johnson⁶ to be a first-order homogeneous reaction and to be inhibited by hydrogen. As would be expected from the absorption spectrum of this hydride Schwarz⁷ obtained no decomposition on irradiating monosilane with a mercury arc, though the hydrides Si₂H₆ and Si₃H₈ were decomposed, giving free hydrogen and brown deposits with the empirical formulæ SiH_{1.3} and SiH_{1.7} respectively.

In preliminary experiments we confirmed Schwarz' observation on monosilane, and were also unable to obtain any measurable decomposition by using a condensed aluminium spark as the light source with times of irradiation up to sixty minutes. By making use of an arc of the discharge tube type (1000 v., 0.18 amp.), giving mercury resonance radiation, however, and by introducing a pool of mercury into the reaction vessel, a relatively rapid reaction, accompanied by an increase in pressure, took place. Free hydrogen was formed and a brown film was deposited which dissolved readily in 30 per cent. sodium hydroxide solution with evolution of hydrogen. The solid reaction product was probably a polymerised unsaturated silicon hydride, or a mixture of such a hydride with amorphous silicon.

The mercury-sensitised decomposition was investigated quantitatively by irradiating a measured pressure of monosilane in a quartz bulb containing mercury for times varying from 15 to 30 minutes. The bulb was then cooled in liquid nitrogen and the uncondensed gas pumped off through a U-tube similarly cooled to retain condensable gas from the dead space of the apparatus. Such gas was distilled back into the reaction vessel and the residual pressure measured. The non-condensable gas (hydrogen) was measured by the decrease in the total pressure after pumping. The gas which had been frozen out by liquid nitrogen was next shown to be pure monosilane by distilling it in vacuum into a small bulb containing 30 per cent. sodium hydroxide solution and fitted with a tap. This bulb was attached to the apparatus by a ground joint and was removed and shaken. The hydrogen formed in the decomposition of the residual silicon hydride was then measured by reconnecting the bulb tube, evacuating the connecting tubes, and measuring the total residual pressure. The hydrogen found was slightly less than four times the volume of the residual gas



³ Duncan and Howe, *J. Chem. Physics*, 1934, **2**, 851.

⁴ Mahncke and Noyes, *J. Amer. Chem. Soc.*, 1935, **57**, 456.

⁵ Scheibe and Grieneisen, *Z. physik. Chem.*, B, 1934, **25**, 52.

⁶ Hogness, Wilson and Johnson, *J. Amer. Chem. Soc.*, 1936, **58**, 108.

⁷ Schwarz and Heinrich, *Z. anorg. Chem.*, 1935, **221**, 277.

Had higher silicon volatile hydrides been present the ratio would have been greater than four (7 : 1 for Si_2H_6).

The final stage of the analysis consisted of removing the hydrogen, and introducing into the evacuated reaction vessel 1-2 c.c. of 30 per cent. NaOH solution, which was contained in a small dropping funnel fused to the reaction system. The pressure of hydrogen liberated by the interaction of the solid reaction product and the alkali was then measured and corrected for the vapour pressure of the alkali solution. The analytical

TABLE II.—PRODUCTS OF THE PHOTO-SENSITISED DECOMPOSITION OF MONOSILANE.

Initial Silane Pressure, mm.	Final Pressure, mm.	Per Cent. SiH_4 Decomposed.	p_{H_2} Formed in Reaction, mm.	p_{H_2} from Solid Product, mm.	Formula of Solid.
105.6	112.0	9.6	16.4	26.0	$\text{SiH}_{0.91}$
39.9	44.7	12.0	9.6	14.7	$\text{SiH}_{0.84}$
59.5	68.5	16.0	18.5	22.7	$\text{SiH}_{0.48}$

results from three experiments are given in Table II. All pressure measurements were made at 15°C ., and the arc was in each case 2 cm. from the quartz bulb.

In these experiments only a small proportion of the monosilane can be decomposed as the solid film formed in the reaction render the quartz vessel opaque to ultra-violet light. The formula of the solid hydride varies from $\text{SiH}_{0.48}$ to $\text{SiH}_{0.91}$ with the extent of the reaction, which indicates that it is a mixture consisting possibly of amorphous silicon and the hydride SiH_2 (cf. Schwarz and Heinrich).⁷

The decomposition of silane at low pressures enabled the reaction to be carried to completion, since the amount of solid deposited was relatively small, and gave a further means of examining the products. The apparatus is shown in Fig. 1. The quartz reaction bulb A (12 cm. long, 2.5 cm. diameter) was attached by a ground joint and the pressures were measured by means of the mirror Bourdon gauge⁸ B. Small quantities of monosilane could be admitted into A by the capillary leak C, both C and B having been previously calibrated against a McLeod gauge. The reaction vessel was irradiated with the mercury resonance arc, which was placed at 2 cm. from the surface of the bulb, containing about 1 c.c. of mercury. The increase in pressure could be followed by the mirror gauge, and it was found that the initial reaction rate was constant but that at a later stage it decreased. This retardation is believed to be due to the deposition of a very thin film of solid reaction product on the quartz. The curves in Fig. 2 illustrate the course of the reaction with time. They are very similar to curves obtained by Simmons and Beckman⁹ for the mercury sensitised

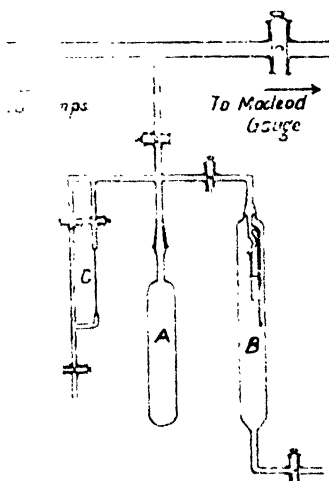


FIG. 1.

⁸ Foord, *J. Scientific Instruments*, 1934, 2, 126.

⁹ Simons and Beckman, *J. Amer. Chem. Soc.*, 1936, 58, 454.

decomposition of arsine into arsenic and hydrogen. The formula of the solid silicon hydride may be calculated from the pressure change in the reaction, and is shown in Table III.

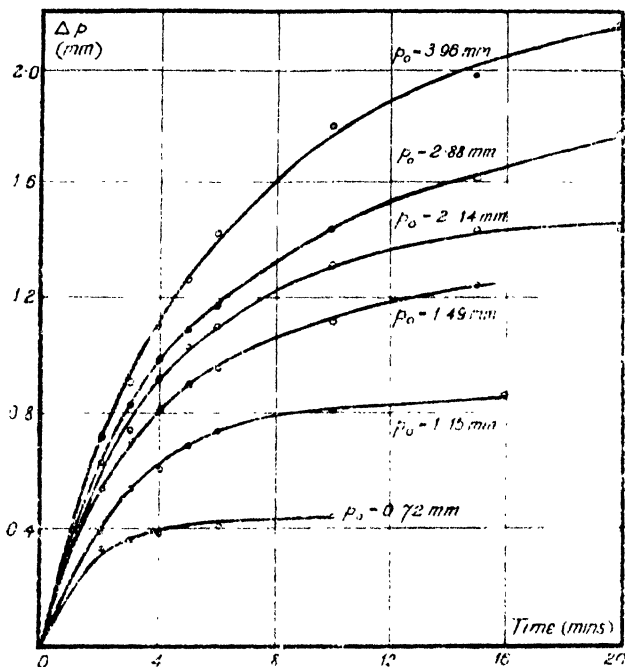


FIG. 2.—Curves showing the rate of the mercury photo-sensitised decomposition of monosilane.

The investigation of the actual reaction mechanism would require a study of the quantum yield and of the effect of hydrogen on the reaction rate. From the point of view of the mechanism of oxidation of silane, however, the primary interest lies in the intermediate formation of radicals, since it is these which are believed to be active in initiating the chain mechanism of the oxidation.

TABLE III.

Initial Silane Pressure, mm.	Final Pressure, mm.	Pressure Increase, mm.	Formula of Solid.
0.72	1.15	0.43	$\text{SiH}_{0.88}$
1.15	2.02	0.87	$\text{SiH}_{0.81}$
1.49	2.67	1.18	$\text{SiH}_{0.48}$
2.14	3.59	1.45	$\text{SiH}_{0.44}$

The Effect of Ultraviolet Light on the Ignition of Monosilane-Oxygen Mixtures.

Experiments on the thermal oxidation of monosilane¹ have shown that mixtures containing 50 to 90 per cent. of oxygen at total pressures between 500 and 100 mm. react explosively in the neighbourhood of 100° C. No reaction was detected with such mixtures above or below the upper and lower critical explosion limits, respectively, or below the critical temperature, which was about 84° C. for a mixture containing 30 per cent. monosilane. In the experiments described below mixtures containing 30 to 50 per cent. silane were exposed to ultraviolet light at room temperature, i.e., some 70° below the minimum temperature for their thermal ignition at

any pressure. Any reaction observed under these conditions must be due to the action of the light in producing active centres in the gas mixture.

The first series of experiments was carried out at low pressures in the apparatus shown in Fig. 1, modified by the inclusion of a second calibrated capillary for the admission of oxygen into the reaction system. Gas mixtures were made up by admitting the two gases simultaneously through their respective capillaries. The composition was varied between 30 and 50 per cent. monosilane. The light sources used were a condensed aluminium spark (10,000 v., 0.3 amp.), a hot mercury arc (110 v., 2.5 amp.), and the mercury resonance arc already described. They were operated for at least ten minutes before use and were placed 10 cms. from the quartz bulb. Each of these sources caused instantaneous ignition of gas mixtures at 15-20° containing between 30 and 50 per cent. of monosilane at pressures from 2 to 11 mm. Ignition was readily detected by a sudden movement of the light spot of the mirror gauge, and also by the appearance of a white film on the quartz bulb. It took place without a measurable time lag even when the light source was removed to a distance of 40 cms., and also when the reaction vessel was screened from direct light but received light reflected from the walls of the room. It is apparent, therefore, that the amount of light needed to produce a positive effect is exceedingly small.

When a thin film of gelatin (limit of transmission 2400 Å) was inserted between the light source and the quartz bulb ignition no longer took place when the aluminium spark was used, but either the hot or cool mercury arc caused an instantaneous explosion provided the reaction vessel contained liquid mercury. The gelatin filter removes completely all radiation of a wavelength absorbed by oxygen, and ignition by the filtered light from the mercury arcs must therefore be due to the action of mercury resonance radiation. It is generally assumed that the uncooled mercury arc gives no 2537 Å. resonance light when it has been in operation for a short time, but in the present case a very small amount of such radiation probably suffices to produce a positive effect.

With the aluminium spark as the light source it was found that insertion of a filter consisting of a 5 cm. thickness of a 5 per cent. solution of sodium chloride in distilled water stopped the reaction completely. No explosion or slow reaction took place at room temperature whatever the pressure of the gas mixture. This filter removes all wavelengths less than 2050 Å., *i.e.*, those which are absorbed by oxygen. Since monosilane has been shown to be transparent down to 1850 Å. we may conclude that absorption of light by molecular oxygen alone is able to initiate explosion. Such light produces excited oxygen molecules in the first place, but may yield oxygen atoms by a secondary process.

At higher pressures (100-500 mm.) a slow reaction was observed on irradiating silane-oxygen mixtures with the mercury resonance arc. The reaction vessel consisted of a cylindrical tube (10 cm. long, 2 cm. diameter) with a side tube which was ground at the open end. To this a quartz window was attached with wax. Monosilane-oxygen mixtures were prepared by distilling the hydride into the reaction vessel, by cooling the lower part in liquid nitrogen, and measuring its pressure on a mercury manometer. It was then frozen out again and the requisite amount of oxygen added, after which the monosilane was allowed to vaporise very slowly, and the total pressure measured. As it was desired to obtain a measurable reaction rate, instead of explosion, on illumination no mercury was placed in the reaction vessel, though a restricted supply would be furnished by the manometer. The mercury resonance arc was placed 4 cm. from the quartz window. This caused only a slight rise in temperature of the reaction vessel.

Under these conditions silane-oxygen mixtures reacted slowly with a pressure decrease, and a white deposit of silica formed on the quartz window. Some typical curves obtained by plotting the pressure decrease against time are shown in Fig. 3. In all cases there was an induction

period, which was greater the higher the initial pressure and the higher the initial oxygen concentration. In the initial stages of the reaction the curves are approximately exponential and satisfy the relationship

$$\Delta p = ke^{\phi t},$$

which is valid in the thermal oxidation of hydrocarbons and other substances. As the reaction proceeds the deposit of silica retards the reaction and prevents an exact kinetic study of the reaction being made.

In no cases were we successful in obtaining a slow reaction culminating in an explosion. If, however, the pressure of the reaction mixture was

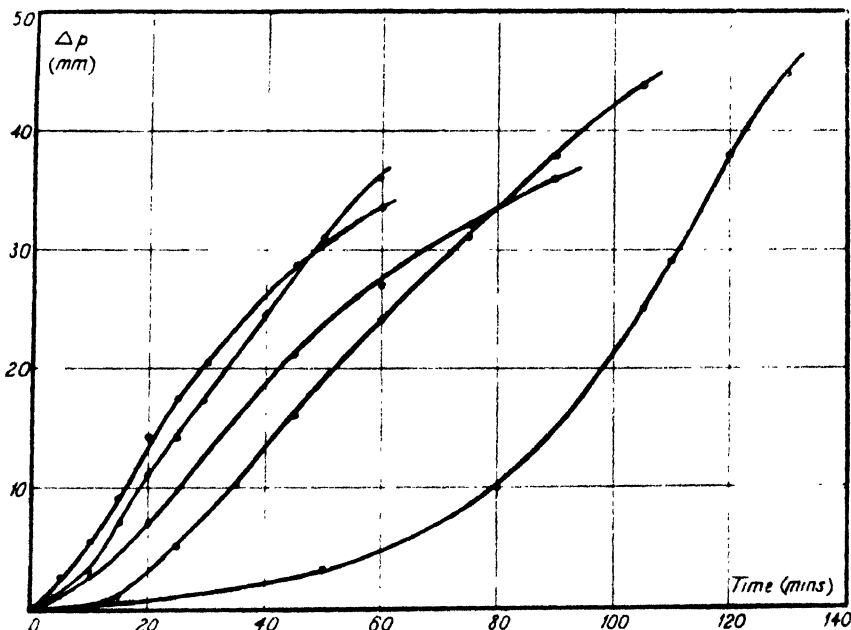


FIG. 3.—Slow oxidation of Monosilane.
Plot of Δp against time.

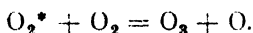
Curve. (right to left.)	Initial pressure mm.	Per cent. SiH_4 .
1	410	23.6
2	252	21.3
3	107	17.6
4	169	24.6
5	110	22.8

slowly reduced immediately after irradiation had been commenced an explosion took place when a certain limiting pressure was reached. Thus, for example, a 16 per cent. mixture at 20°C . at an initial pressure of 580 mm. exploded when the pressure was reduced to 66 mm. during irradiation. Such a mixture would not explode at any pressure if it were not irradiated; indeed, our previous observations have shown that the temperature would have to exceed 80°C . before ignition would take place on reducing the pressure. The effect of light is therefore to lower the ignition temperature for this mixture at a given pressure by 60°C .

Discussion.

The effect of ultraviolet light on the upper critical explosion limit of monosilane-oxygen mixtures is similar to that first observed by Hinshelwood and Clusius¹⁰ in the case of the lower critical oxidation limit of phosphine-oxygen mixtures and afterwards studied in greater detail by Melville,^{11, 12} for both the upper and lower critical limits. Hinshelwood and Clusius found that when irradiated, phosphine oxygen mixtures exploded at a lower pressure than the normal critical limit, which was of the order of a few mm. It was shown that irradiation produced an active substance, and that the activity and the consequent lowering of the lower explosion limit persisted for some time after irradiation was stopped. The effective wavelengths were between 2500 and 2800 Å. Such light is not absorbed by phosphine¹³ and it is possible that the active light was the mercury resonance line 2537 Å. Melville¹⁴ proved that the lowering of the explosion limit of phosphine-oxygen mixtures by irradiation with a mercury arc was due to a change in the surface of the reaction vessel: indeed, the phenomenon could be reproduced by pretreating the walls with atomic hydrogen.

The experiments on the irradiation of silane-oxygen mixtures differ from those with phosphine in one important respect, namely, that monosilane does not absorb light of wavelength greater than 1850 Å. Accordingly the initiation of explosion by irradiation with the aluminium spark is an unambiguous case of a chain reaction initiating by exciting only the oxygen molecules. The observations are consistent with the reaction mechanism given (p. 1577), for atomic oxygen can be formed by the process



Alternately it is possible for excited molecular oxygen to initiate the oxidation of monosilane. The mechanism advanced is admittedly tentative, and the kinetic analysis of the results on the thermal oxidation¹ would be equally valid if the two active centres propagating the chain were O_2^* and SiH_2 . We hope, however, to carry out further experiments to differentiate between the effects of molecular and atomic oxygen in initiating these reactions.

Summary.

- (1) Monosilane, disilane, and trisilane absorb light of wavelengths < 1850, < 1980-2020, < 2140-2190 Å. respectively.
- (2) Monosilane mixed with mercury vapour is decomposed by the 2537 Å. mercury resonance line, giving hydrogen and a solid reaction product consisting of a polymerised hydride SiH_x ($x < 0.9$) or a mixture of silicon and such a polymer.
- (3) Monosilane-oxygen mixtures at temperatures below the normal range for thermal ignition may be caused to explode by irradiation with light from an aluminium spark or a mercury resonance arc.
- (4) Monosilane-oxygen mixtures at pressures above the critical explosion pressure undergo a slow oxidation on exposure to the unfiltered light from a mercury resonance arc. This reaction has an induction period, and, in

¹⁰ Hinshelwood and Clusius, *Proc. Roy. Soc., A*, 1930, **129**, 589.

¹¹ Melville, *ibid.*, 1933, **139**, 541.

¹² Melville, *J. Chem. Physics*, 1934, **2**, 739.

¹³ Cheesman and Emeléus, *J.C.S.*, 1932, 2847.

¹⁴ Melville, *Proc. Roy. Soc., A*, 1932, **138**, 390.

its initial stages, follows the exponential law $\Delta p = ke^{kt}$ which characterises hydrocarbon combustion.

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THE OXIDATION OF CARBON—PART II.

By J. D. LAMBERT.

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Two types of process possible in the oxidation of carbon are :

(1) Direct formation of carbon dioxide by impact of oxygen molecules on a clean carbon surface.

2. Primary formation of both carbon dioxide and carbon monoxide by the breakdown of surface oxide complexes.

It was shown in a previous paper¹ that in the temperature range 250-500° C. pure carbon is oxidised by process (1) alone; whilst the presence of iron in the carbon blocks process (1) and oxidation proceeds exclusively by process (2). The latter reaction is complicated by a secondary conversion of carbon monoxide to carbon dioxide which masks the proportion in which the two products are initially formed and in default of information as to the constancy or simplicity of this proportion the exact mechanism of the oxidation process was obscure. Further experiments have been made in order to throw light upon this problem. The first stage was to investigate the conversion of carbon monoxide to carbon dioxide: the second stage to try to eliminate this secondary effect in the light of the information obtained.

The experimental method was that previously described¹ and the same apparatus and materials were used. The carbon monoxide was obtained from a cylinder, and was shown by analysis to contain not more than 3 per cent. of impurity (approximately 1 per cent. carbon dioxide, 1.5 per cent. oxygen and 0.5 per cent. nitrogen). This was less pure than the oxygen and nitrogen used, which were usually 99.5 per cent. pure, and the experimental accuracy which could be obtained when using carbon monoxide was correspondingly lower.

The Conversion of Carbon Monoxide to Carbon Dioxide on the Carbon Surface.

The conversion of carbon monoxide to carbon dioxide was investigated on coconut charcoal, graphite, anthracite, and iron treated coconut charcoal by passing mixtures of carbon monoxide and nitrogen, carbon monoxide and oxygen, and nitrogen and oxygen over the carbon at various temperatures and analysing the products. It was found that in no case is there any conversion of carbon monoxide to carbon dioxide *except in the presence of oxygen*. The process therefore appears to be an oxidation and not, as was previously supposed, an autoxidation. The results obtained with mixtures of carbon monoxide and oxygen are shown in Table I. Comparison of the products obtained from a carbon monoxide-oxygen mixture

¹ Lambert, *Trans. Faraday Soc.*, 1936, **32**, 452.

TABLE I.—OXIDATION OF CARBON MONOXIDE.

Type of Carbon.	Temp.	Flow Rate. c.c./min.	Initial Percentage.			Final Percentage.		
			O ₂	N ₂	CO.	CO ₂	O ₂	CO.
<i>Coconut</i>	266° C.	8.02	46.4	53.6	0	17.9	26.3	2.2
			46.4	0	53.6	17.4	28.9	53.65
<i>Charcoal.</i>	446° C.	8.02	46.4	0	53.6	> 90.0	—	—
	369° C.	8.02	46.4	0	53.6	51.7	2.03	46.3
	253° C.	8.02	46.4	0	53.6	13.9	32.8	53.3
<i>Graphite.</i>	453° C.	8.02	46.4	0	53.7	> 90.0	—	—
<i>Anthracite.</i>	387° C.	8.01	46.3	53.7	0	12.9	28.0	4.4
			46.3	0	53.7	16.3	28.2	55.5
			46.3	0	53.7	16.3	28.85	54.9
			46.3	53.7	0	13.7	28.5	5.5
	460° C.	7.97	46.3	0	53.7	49.5	1.81	48.9
			46.3	53.7	0	37.6	1.7	10.55
	414° C.	8.04	54.3	45.7	0	24.05	14.6	8.2
			53.2	0	46.8	30.6	14.0	55.3
<i>Iron-treated Coconut Charcoal.</i>	411° C.	8.11	47.4	0	52.6	10.5	33.6	55.9
			47.4	52.6	0	10.7	32.6	5.3
	562° C.	8.05	47.2	0	52.8	45.7	2.01	52.4
			45.6	54.4	0	28.6	1.5	22.7

with those obtained under the same conditions from a nitrogen-oxygen mixture containing the same percentage of oxygen shows clearly whether or not oxidation of carbon monoxide is taking place but is insufficiently accurate to give information about the kinetics or mechanism of the reaction. It is not possible with the experimental accuracy available to sort out the results of primary carbon oxidation, secondary oxidation of the carbon monoxide produced and primary oxidation of the carbon monoxide initially present together with the accompanying volume changes. The qualitative information which is obtained however enables several important conclusions to be drawn.

Discussion in Relation to Previous Results.

The small temperature range over which experiments could be made on the kinetics of oxidation of each form of carbon used was arbitrarily determined by the relation between rate of reaction and the available rates of gaseous flow.¹ The experiments on coconut charcoal were made in the neighbourhood of 260° C., those on graphite 450° C., on anthracite

and on iron treated charcoal 380-390° C. Under these conditions graphite and coconut charcoal were oxydised to carbon dioxide, and anthracite and iron treated coconut charcoal to a mixture of carbon dioxide and carbon monoxide with the proportion of carbon dioxide increasing with the time of reaction. Table I. shows that although rapid oxidation of carbon monoxide takes place on coconut charcoal at higher temperatures there is no trace of this at 260° C. so that the assumption which was previously made that carbon dioxide is the sole primary product of reaction is justified. In the case of graphite rapid oxidation of carbon monoxide does take place at 450 °C. but the very close resemblance of the reaction kinetics with those shown by coconut charcoal, together with the fact that no trace of carbon monoxide is found in the reaction product gives some justification to the same assumption. Anthracite, as was to be expected, shows a definite though not very rapid oxidation of carbon monoxide at 387° C., which is sufficient to account for the variation in the composition of the oxidation product, and a much more rapid oxidation of carbon monoxide at higher temperatures. The iron treated charcoal shows considerable oxidation of carbon monoxide at higher temperatures but no appreciable effect at 411° C., although when oxydised at 390° C. its behaviour was similar to that of anthracite: possibly different samples vary in this respect. The oxidation of both of these latter charcoals gave an apparent course of total reaction with time approximating closely to first order.¹ As the conversion of carbon monoxide to carbon dioxide is an oxidation and not an autoxidation ($2\text{CO} \rightarrow \text{CO}_2 + \text{C}$) as was previously assumed, the secondary process will increase the total percentage of oxygen which has reacted. The approximation to first order is, therefore, fortuitous as with increasing time of reaction a considerable proportion of the observed percentage reaction must be attributed to secondary oxidation of carbon monoxide. The rate of the primary reaction must fall off with time more rapidly than the observed rate and the primary reaction must be of an order higher than first. This is in complete accordance with the views put forward later.

Experiments on Manganese Treated Charcoal.

General inspection of Table I. shows that at high temperatures carbon monoxide undergoes oxidation much more rapidly on coconut charcoal and on graphite than on anthracite and iron treated charcoal. It would appear that the presence of iron on the carbon inhibits the surface oxidation of carbon monoxide to a large extent. This suggested that it might be

TABLE II.—COURSE OF REACTION WITH TIME.

Temperature 389° C. Initial Oxygen Concentration 36 Per Cent.

Flow-rate. $= \frac{V}{t}$.	Percentage Reaction.			Second Order Reaction Constant.	$\frac{\text{CO}_2}{\text{CO}}$
	To CO_2 .	To CO^* .	Total.		
c.c./min.					
9.89	13.2	3.7	16.9	2.01×10^{-2}	1.82
4.94	22.2	5.8	28.0	1.92×10^{-2}	1.91
3.29	28.9	7.5	36.4	1.88×10^{-2}	1.94
9.89	12.8	3.2	16.0	1.88×10^{-2}	1.98

* The "percentage reaction to CO" is half the actual percentage CO found.¹

possible to find another "promoter" which would show the same effect as iron and in addition inhibit completely the secondary carbon monoxide oxidation at a temperature when the primary combustion took place at a measurable rate; thus enabling investigation of the true composition of the primary reaction product. It was found that a sample of coconut charcoal treated with manganous chloride by a process identical to the previously described treatment with ferric chloride¹ fulfilled the required conditions, and experiments with this charcoal are described below.

The charcoal undergoes oxidation at roughly the same conditions of temperature and rate as anthracite and iron promoted charcoal to a mixture of carbon dioxide and carbon monoxide.

The Course of Reaction with

Time is shown by Table II. and is approximately described by a second order equation. The ratio of carbon dioxide to carbon monoxide in the product is almost constant and independent of the time of reaction.

The effect of Initial Oxygen Concentration is shown in Fig. 1. The percentage reaction in a given time decreases a little with increasing

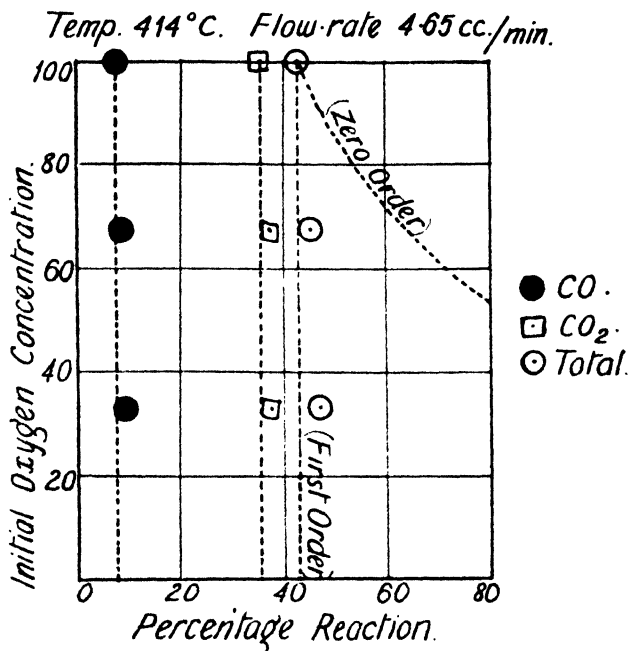


FIG. 1.—Effect of Initial Oxygen Concentration.

TABLE III.—EFFECT OF CARBON DIOXIDE.

Temperature, 409.5° C. Rate of Flow, 9.56 c.c./min.

Initial.			Final.	
Percentage O ₂ .	Percentage N ₂ .	Percentage CO ₂ .	Percentage CO ₂ .	Percentage CO.
35.8	64.2	0	7.0	1.5
35.0	0	64.2	71.5	1.43

oxygen concentration: behaviour which would be shown by a reaction of slightly less than first order. The composition of the product is almost constant.

The Energy of Activation is approximately 23,000 cal. (cf. Coconut Charcoal $E = 29,000$ cal., Anthracite $E = 31,000$ cal.). Fig. 2 shows $\log k$ (calculated as for a second order reaction) plotted against the reciprocal of the absolute temperature.

The Effect of Carbon Dioxide is shown in Table III. At 409° C. there is no retardation and no reduction to carbon monoxide.

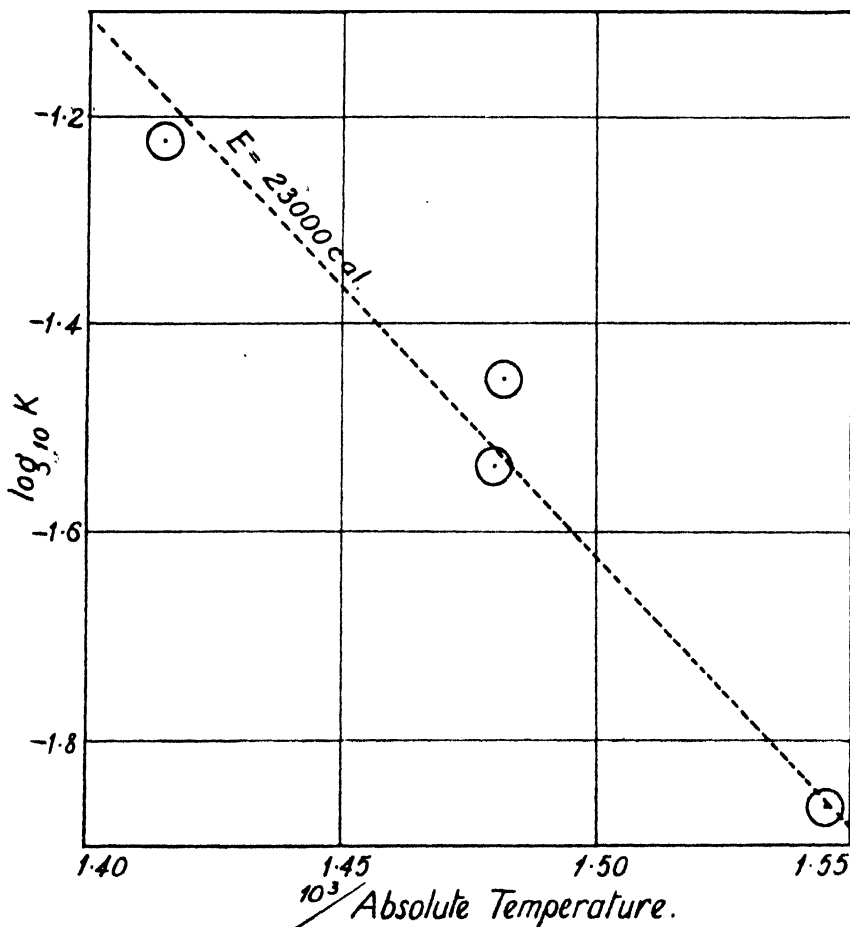


FIG. 2.—Effect of Temperature.

The Effect of Carbon Monoxide is shown in Table IV. At 405° C. there is no oxidation to carbon dioxide, and the carbon monoxide has no

TABLE IV.—EFFECT OF CARBON MONOXIDE.

Temp.	Rate of Flow. c.c./min.	Initial Percentage.			Final Percentage.		
		O ₂ .	N ₂ .	CO.	CO ₂ .	O ₂ .	CO.
405° C.	7.91	47.8	52.2	0	14.5	29.7	3.5
		47.8	0	52.2	15.0	28.9	56.1
517° C.	7.97	48.1	0	51.9	28.2	14.6	57.2
		48.1	51.9	0	23.7	14.5	14.5

effect on the reaction, the percentage of carbon dioxide formed remaining unchanged when carbon monoxide is substituted for nitrogen in the initial mixture. At a higher temperature 517° C. definite oxidation to carbon dioxide has set in.

The variation of the composition of the reaction product under different conditions is shown in Table V. The experimental data in this table

TABLE V.—COMPOSITION OF REACTION PRODUCT.

Mixtures of Oxygen and Nitrogen.

Temp.	Rate of Flow. c.c./min.	Initial Percentage O ₂	Product.		CO ₂ CO
			Percentage CO ₂	Percentage CO	
389° C.	9.89	36.5	4.55	2.3	1.98
530° C.	9.87	36.6	14.8	10.4	1.42
	3.25	37.0	21.65	12.14	1.78
402° C.	10.1	35.5	7.1	3.7	1.92
374.5° C.			3.36	1.75	1.92
432.5° C.			9.9	5.6	1.78
403° C.			6.2	3.2	1.94
478° C.	10.08	35.8	12.95	7.7	1.68
	3.34	36.6	20.7	10.0	2.07
430° C.	10.13	35.6	9.67	4.9	1.97
	3.36	35.5	17.3	8.3	2.08
443° C.	10.17	36.1	11.05	5.53	1.90
	3.06	36.5	18.7	9.2	2.03
460° C.	3.05	36.3	19.7	9.7	2.03
	10.14	36.1	12.2	6.8	1.80
417° C.	10.14	36.0	8.24	3.7	2.22
407° C.	9.95	34.7	6.6	3.7	2.25
	3.30	34.2	13.56	5.96	2.28

were all given by a single sample of charcoal and are arranged in the order in which they were obtained. At temperatures between 370° C. (the lowest temperature at which measurable oxidation took place) and 430° C. the ratio of carbon dioxide to carbon monoxide is independent of the time of reaction and approximately constant between $\text{CO}_2/\text{CO} = 1.9 - 2.0$. There is a tendency for the proportion of carbon dioxide to increase as the charcoal burns away: the last value of the ratio taken at 407° C. is 2.28. At temperatures above 430° C. the proportion of carbon monoxide begins to show a definite increase, partially masked by the simultaneous setting in of secondary carbon monoxide oxidation.

Discussion.

The kinetics of the oxidation of manganese treated charcoal show a course of reaction approximating to second order, and an effect of initial oxygen concentration approximating to first order. This can be interpreted in terms of a reaction of an order between first and second with respect to oxygen and retarded by the reaction products, following an expression of the form:

$$\frac{d[\text{products}]}{dt} = \frac{k[\text{O}_2]^x}{1 + b[\text{products}]}$$

If " x " has a value between one and two the retardation factor " b [products]" will cause the rate to fall off more rapidly with time than it would otherwise do, thus increasing the apparent order of reaction towards two; whilst the accelerating effect of an increase of the initial oxygen concentration will be counterbalanced by an increase in b [products], diminishing the apparent order towards one. An order between first and second would be shown by a mechanism involving the breakdown of an incomplete surface oxide layer on impact of oxygen molecules from the gas. The oxide layer being incomplete, its extent will be proportional to a fractional power of the oxygen pressure and:

$$\begin{aligned} \text{Rate of reaction} &= k \times (\text{number of impacts of gaseous oxygen molecules on surface oxide layer}). \\ &= k \times [\text{O}_2] \text{ (amount of surface oxide)}. \\ &= k'[\text{O}_2][\text{O}_2]^n = k'[\text{O}_2]^{(1+n)} \end{aligned}$$

" n " being a fraction less than unity.

Such a mechanism is in accordance with the views previously expressed and with the experimental results *except* in so far as Tables III. and IV. show no trace of retardation by either carbon monoxide or carbon dioxide. It is difficult to find any alternative explanation of the kinetics, and this suggests that the primary product which gives retardation is due to something other than free carbon dioxide or carbon monoxide which gradually accumulates on the surface.

It is interesting to note that the carbon suboxide described by Klemenc,² decomposes at 400° C. to give carbon monoxide and carbon dioxide in ratios varying from $\text{CO}_2/\text{CO} = 2.12 - 1.86$ which are in striking agreement with the values given in Table V. for temperatures in this region. The proportion of carbon monoxide produced by decomposition of the suboxide increased with rise of temperature, as was found in our experiments, reaching a value of $\text{CO}_2/\text{CO} = 1.0$ at 500° C. This cannot be compared with values in Table V., as considerable secondary oxidation of carbon monoxide had set in before this temperature, but the ratios found at 530° C. are not incompatible with a primary ratio of 1:1. There is scarcely sufficient justification for supposing that carbon suboxide itself is the primary product of oxidation of manganese treated charcoal in view of the very complex phenomena involved in its decomposition and the difficulty of predicting their influence on the kinetics of the reaction, but considerable similarity clearly exists between the two cases.

All the above considerations may be applied equally to the phenomena observed with anthracite and iron-promoted coconut charcoal if the secondary oxidation of carbon monoxide is taken into account.

² Klemenc, Wechsberg and Wagner, *Z. physik. Chem.*, A, 1934, 170, 9

Summary.

Previous work¹ had shown that carbon containing iron is oxydised at 400° C. to give a mixture of carbon dioxide and carbon monoxide as primary product. The reaction mechanism is obscured by secondary conversion of carbon monoxide to carbon dioxide, which masks the ratio in which the two gases are initially formed. Further investigation has been made of this secondary process, which has been shown to be an *oxidation* occurring more rapidly on a clean carbon surface than on a carbon surface containing iron. The earlier experimental results are discussed in the light of the information obtained.

It has been found that coconut charcoal treated with manganese shows similar behaviour to iron treated charcoal on oxidation at 400° C. but *without* secondary oxidation of carbon dioxide monoxide.. The oxidation of this charcoal has been fully investigated with special reference to the composition of the product, and the reaction mechanism is discussed. It appears possible that a gaseous complex similar to carbon suboxide² is the primary product of oxidation.

The author is very grateful to Mr. C. N. Hinshelwood for his interest in the whole of this work.

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THE VAPOUR PRESSURE AND HEAT OF SUBLIMATION OF CARBON.

BY PAUL GOLDFINGER AND WILLIAM JEUNEHOMME.

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1. The value usually accepted for the heat of sublimation (vaporisation) of carbon, corresponding to the process

$$C_{\text{diamond}} = C(^3P)_{\text{gas}} - L_C \quad . \quad . \quad . \quad (1)$$

at 0° K is $L_C \sim 150$ kcal.¹ This value was obtained originally by K. Fajans² from the vapour pressure measurements of H. Kohn and M. Guckel.³ Their method is, however, very indirect, and their results seemed to be in disagreement with those of other authors.⁴ Besides, it is necessary to consider the fraction of C_2 in the carbon vapour⁵ and the data necessary to calculate the equilibrium



are very incomplete.

¹ E.g., R. G. W. Norrish, *Trans. Faraday Soc.*, 1934, **30**, 103.

² *Z. Elektrochemie*, 1925, **31**, 60; *Z. Physik*, 1920, **1**, 101.

³ *Ibid.*, 1924, **27**, 307.

⁴ Of the numerous references given in the International Critical Tables on the vapour pressure of carbon only three, except the work of Kohn and Guckel, concern experimental determinations: (a) Wertenstein and Jedrzejewski, *Comptes rendus*, 1923, **177**, 316; (b) A. Thiel and F. Ritter, *Z. anorg. Chemie*, 1924, **132**, 125; (c) E. Ryschkewitsch, *Z. Elektrochemie*, 1925, **31**, 54; see also A. L. Marshall and F. J. Norton, *J. Amer. Chem. Soc.*, 1933, **55**, 431.

⁵ G. B. Kistiakowsky and W. E. Vaughan, *Physic. Rev.*, 1932, **40**, 47.

Several authors have therefore sought to obtain a more exact value of L_C from thermochemical cycles.⁶ However, only the relation⁷

$$L_C = D_{CO} - 86.3 \pm 0.2 \text{ kcal. (86.3 kcal.} = 3.74 \text{ v.)} \quad (2)$$

between L_C and the energy of dissociation, D_{CO} , of the normal CO molecule to normal C and O atoms is sufficiently accurate to permit an improvement of the former value.

A few other magnitudes, related to D_{CO} , and therefore to L_C , were given recently by P. Goldfinger, W. Lasareff and B. Rosen.⁸

It may be useful to emphasise that older spectroscopic data on D_{CO} were rather uncertain: the value given by R. S. Mulliken for example⁹ was obtained from "thermochemical data," i.e., probably from L_C : to use this value, as certain authors have done, to obtain L_C from D_{CO} is of course a *circulus vitiosus*.

2. Recently considerable progress has been made concerning the spectroscopic value of D_{CO} .

D. Coster and F. Brons¹⁰ as well as R. Schmid and L. Gerö¹⁰ have observed predissociation in $v = 0, J = 38$ and $v = 1, J = 18$ of the $B^1\Sigma$ level of carbon monoxide. The asymptote of the perturbing electronic level lies according to B. Rosen¹¹ at 11.06 ± 0.005 v. We have therefore

$$D_{CO} = 11.06 \pm 0.005 - E \text{ v.} \quad (3)$$

where E is the sum of the electronic activation energies of the dissociation products of the perturbing level.

Three values in agreement with equation (3) were discussed by Goldfinger, Lasareff and Rosen;⁸

TABLE I.—SPECTROSCOPIC VALUES OF THE DISSOCIATION ENERGY OF CARBON MONOXIDE (D_{CO}) AND CORRESPONDING VALUES OF THE HEAT OF SUBLIMATION OF CARBON (L_C).

	I.	II.	III.
D_{CO}	11.06	9.10	8.39 v.
L_C	168.8	123.6	107.2 kcal.

these and the corresponding values of L_C are given in Table I.

There is only one intermediate value, $D_{CO} = 9.81$ v., but this is, according to D. Coster and F. Brons¹⁰ in disagreement with the data on the $A''\Pi$ level of CO; other intermediate values, as for example $D_{CO} = 10.4$ v.¹² are in disagreement with equation (3), because there are no other electronic levels of C and O, with small activation energy, except 1D and 1S , and these were con-

sidered in Table I. in all combinations.

In a preliminary note, Goldfinger and Lasareff⁷ have proposed the value $D_{CO} = 11$ v., the corresponding value of L_C being in best agreement with the usually accepted data; as will be shown here, the vapour pressure curve of carbon, calculated from this value is in sufficiently

⁶ E.g., G. B. Kistiakowsky and H. Gershinowitz, *J. Chem. Physics*, 1933, **1**, 432.

⁷ F. D. Rossini, *Bureau of Standards J. Res.*, 1934, **13**, 21; P. Goldfinger and W. Lasareff, *Nature*, 1935, **135**, 1077.

⁸ P. Goldfinger, W. Lasareff and B. Rosen, *Comptes rendus*, 1935, **201**, 958; cf. also *Comptes rendus du 2me Congres National des Sciences*, Bruxelles, 1935.

⁹ R. S. Mulliken, *Rev. Modern Physics*, 1932, **4**, 1.

¹⁰ D. Coster and F. Brons, *Physica*, 1934, **1**, 155, 634; R. Schmid and L. Gerö, *Z. Physik*, 1935, **93**, 656; **96**, 198, 546.

¹¹ *Nature*, 1935, **136**, 226.

¹² R. Lessheim and H. Samuel, *ibid.*, **136**, 606.

good agreement with the data of Kohn and Guckel and the discrepancy with those of Ryschkewitsch, Wertenstein and Jedrzejewski as well as Marshall and Norton⁴ can easily be explained.

However, from the spectroscopic standpoint, the value $^{18} D_{CO} = 9.10$ v. first proposed by Rosen⁴ seemed much more satisfactory. In fact, this value gives for the dissociation energy of the $A^1\Pi$ level 4.3 v., whereas the former value would give 3.07 v.; the extrapolated value is about 4 v., vibrational levels being observed up to 2.41 v. Moreover, the missing of the higher vibrational levels of the $B^2\Sigma$ state can only be explained if there is a perturbing level with an asymptote below 11 v. Therefore $D_{CO} = 9.10$ v. was accepted by Goldfinger, Lasareff and Rosen,⁸ who have shown also that different magnitudes, which are related to D_{CO} are in much better agreement with this value, than with the value $D_{CO} = 8.39$ v. proposed by Coster and Brons and Schmid and Gerö.

The present paper was practically concluded, when Brons¹⁴ published results concerning a predissociation at 9.68 v. and Schmid and Gerö¹⁵ on a predissociation at 9.57 v. This is a definite argument against the value $D_{CO} = 11.06$ v.; although the arguments of Brons as well as of Schmid and Gerö in favour of $D_{CO} = 8.4$ v. are not considered as definite by G. Herzberg,¹⁶ who also proposes $D_{CO} = 9.1$ v. His considerations, as well as those of Goldfinger, Lasareff and Rosen⁸ can be applied *a fortiori* to the value 6.9 v. proposed by Schmid and Gerö.¹⁵

It seemed possible to improve considerably the accuracy of the discussion, by calculating, by the methods of statistical mechanics the vapour pressure curves for the three values of L_C given in Table I. These curves are sufficiently different to make a decision between them possible even with rather rough experimental data. This would permit us then to obtain finally, by equations (2) and (3), a value of L_C , which must be exact within less than 0.5 kcal.

3. The equilibrium pressure of monatomic carbon vapour, considered as an ideal gas, in presence of solid or even liquid carbon can be calculated with an accuracy which is certainly much higher than could be obtained by any direct measurement, supposing, of course, that a decision between the three values of L_C given in Table I. is possible.

(a) The molal free energy (F_1^0) of monatomic carbon vapour is given in the notations of F. W. Giaque¹⁷ by

$$\frac{F_1^0 - E_{0,1}^0}{T} = R \log_e P_1 - 3/2 R \log_e M_1 - R \log_e Q_1 - (5/2 R \log_e T + C + R \log_e R) \quad (4)$$

where $E_{0,1}^0$ is the zero point energy of carbon gas, $R = 1.986$ cal. the gas constant per mole, $C = R \log_e \frac{(2\pi k)^{3/2}}{h^3 \cdot N^{5/2}} = -16.024$ the Sackur constant and $M = 12.00$ the atomic weight of carbon;

$$Q_1 = 9 + 5 \cdot e^{-28,800/RT} + \dots$$

¹⁸ Instead of this value ¹¹ Goldfinger and Lasareff⁷ gave first $D_{CO} = 8.79$ v., from an extrapolation of the $A^1\Pi$ level, since the exact value of the asymptote (11.06 v.) was not then known.

¹⁴ *Nature*, 1935, **136**, 796; *Physica*, 1935, **2**, 1108; see, however, L. Gerö, *Z. Physik*, 1936, **99**, 52.

¹⁵ R. Schmid, *ibid.*, 1936, **99**, 274; R. Schmid and L. Gerö; *ibid.*, 1936, **99**, 287.

¹⁶ Letter to the editor of *Nature*, 1936, **137**, 620; cf. also a detailed discussion by Herzberg to be published soon. By the kindness of Professor Herzberg, we were able to see the manuscript before publication.

¹⁷ *J. Amer. Chem. Soc.*, 1930, **52**, 4808.

is the partition function for the electronic levels of the carbon atom (the second term already represents only a correction of about 1 per cent. at 4000° K. and 2.5 per cent. at 5000° K., and was therefore neglected).

The right-hand side of equation (4) is simply obtained by adding the values of the function $\frac{5}{2} R \log_e T + C + R \log_e R$, given by Giauque (*loc. cit.*¹⁷ p. 4827) the practically constant value

$$R \log_e 12.00 + R \log_e Q_1 = 11.768$$

entropy units (cal./degree).

(b) The free energy (F_2^0) of solid graphite is given by the classical formula

$$\frac{F_2^0 - E_{0,2}^0}{T} = \frac{1}{T} \int_0^T c_p dT - \int_0^T \frac{c_p}{T^2} dT \quad (5)$$

where c_p is the specific heat at constant pressure. For the specific heats up to 2500° K. we have used the data of the International Critical Tables: from 298.1° to 1200° K. the formula of A. Magnus¹⁸ and from 1200° to 2500° the formula of Worthing.¹⁹ Above 2500° Fajans estimated $c_p = 6.5$ cal. for solid carbon up to the melting-point, which lies at 3800° K.,²⁰ and $c_p = 8$ cal. for liquid carbon: we used the former value from 2500° to 3800° K. and the latter value from 3800° upwards. Moreover, at these high temperatures even a considerable error in c_p does not appreciably influence the value of the vapour pressure.

Above the melting-point the gas is in equilibrium with liquid carbon: according to the Clausius-Clapeyron equation the free energy obtained from equation (5) must be corrected to give the free energy of liquid carbon F_1^0 :

$$\frac{F_1^0}{T} = \frac{F_2^0}{T} + \frac{\lambda \cdot (T - 3800^\circ)}{T \cdot 3800} \quad (5a)$$

λ the heat of fusion at 3800° is not known. Fajans² made an estimate of $\lambda \sim 8$ kcal., on the basis of a rule for melting-points and heats of fusion analogous to Trouton's rule. According to this rule, it seems to us safer to take $\lambda \sim 13$ kcal. although an error of 50 per cent. in λ introduces in the calculated equilibrium pressure only an error of about 10 to 15 per cent. between 4000 and 4500° K.

(c) The equilibrium condition is $F_2^0 = F_1^0$ (and above the melting-point $F_1^0 = F_1^*$); $R \lg_e P_1$ is given by the difference of equations (4) and (5), where $E_{0,2}^0 - E_{1,1}^0 = L_C$. Table II. gives the values of $\log_{10} P_1$ for the three different values of L_C .

For the right value of L_C up to about 3000° K. the $\log_{10} P_1$ values are probably accurate within about ± 1 per cent. In Table II. we have given for comparison with our values of $(F^0 - E_0^0)/T$ for graphite those of O. Clayton and F. W. Giauque;²¹ the slight differences seem to be within the accuracy mentioned above. A zero point entropy of graphite as suggested by A. R. Gordon²² would change $\log_{10} P_1$ by about 0.1, i.e., P_1 by about 25 per cent. for all temperatures; nevertheless, even very exact vapour pressure measurements can decide this question only if our knowledge on the equilibrium (1a) is considerably improved. Above 3000° K. the calculations become uncertain, and it is possible that an

¹⁸ *Ann. Physik*, 1923, **70**, 303.

¹⁹ *Physical Rev.*, 1918, **12**, 199.

²⁰ Ryschkewitsch⁴ and H. Alterthum, W. Fehse and M. Pirani, *Z. Elektrochemie*, 1925, **31**, 313.

²¹ *J. Amer. Chem. Soc.*, 1932, **54**, 2623.

²² *J. Chem. Physics*, 1933, **1**, 308.

error is introduced which increases with temperature and reaches about 10 to 15 per cent. near 5000° K.

TABLE II.—EQUILIBRIUM PRESSURE OF MONATOMIC CARBON VAPOUR IN PRESENCE OF GRAPHITE FOR DIFFERENT VALUES OF THE HEAT OF EVAPORATION.

Temperature °K.	$\frac{F_2^\circ - E_2^\circ}{T}$		$\log_{10} P_1$ (Atmospheres).		
	Our Calculation.	Glaueque and Clayton.	$L_0 = 168.8$.	$L_0 = 123.6$.	$L_0 = 107.2$
298.1	0.545	0.545	—	—	—
1200	3.482	3.391	—	—	—
2000	5.427	5.394	- 10.381	- 5.407	- 3.647
2500	6.424	6.411	- 6.671	- 2.692	- 1.284
3000	7.314	7.309	- 4.208	- 0.892	+ 0.281
3500	8.103	—	- 2.459	+ 0.383	+ 1.389
4000	8.81	—	- 1.19	+ 1.30	+ 2.18
4500	9.47	—	- 0.26	+ 1.97	+ 2.73
5000	10.01	—	+ 0.50	+ 2.50	+ 3.20

For the subsequent discussion it may be useful to remark that even if somewhere above 2500° K. (limit of Worthings measurements) a hitherto unknown transformation point of graphite should occur, an error of 0.3 to 0.5 units in $\log_{10} P_1$ seems already very improbable, as can be seen by equation (5a).

(d) The equilibrium (1a) can only be evaluated very roughly, because the value of D_{C_2} is quite uncertain. The free energy F_2° of C_2 molecules is given by an expression of the same form as equation (4), except that here $Q = Q_e + Q_v + Q_r$, where Q_e , Q_v and Q_r are the partition functions of the electronic, vibrational, and rotational energy of the C_2 molecule.

Since the calculation cannot be done exactly, it seems sufficient to consider only the lowest $^3\Pi$ state of multiplicity 6 and use for Q_v the Einstein formula $Q_v = \frac{I}{1 - e^{\theta/T}}$ with $\theta = 2333^\circ$ and $^{23} Q_r = \frac{8\pi^2 \cdot I kT}{2h^2}$ with $I = 34.07 \times 10^{-40}$ c.g.s. The equilibrium condition is $2F_1^\circ = F_2^\circ$, this gives

$$-R \log_e K = -R \log_e \frac{P_2}{P_1^2} = \frac{3}{2} R \log_e M_1 + \left(\frac{5}{2} R \log_e T + C + R \log_e R \right) \\ - \frac{3}{2} R \log_e 2 + R \log_e 9 - R \log_e Q_v - R \log_e Q_r - \frac{2E_{0,1}^\circ - E_{0,2}^\circ}{T},$$

where $2E_{0,1}^\circ - E_{0,2}^\circ = D_{C_2}$, the dissociation energy of C_2 into two normal carbon atoms. Table III. gives the $\log_{10} K$ values for $D_{C_2} = 125$ kcal.

TABLE III.—EQUILIBRIUM CONSTANT OF THE EQUILIBRIUM $C_2 = 2C - D_{C_2}$. CALCULATED FOR $D_{C_2} = 125$ KCAL.

T° K.	2000	2500	3000	3500	4000	4500	5000
$\log_{10} K$	8.5	5.8	4.0	2.7	1.8	1.1	0.5

4. In the figure we have plotted the three sets of calculated values of $\log_{10} P_1$ against $1/T$ (curves a) as well as the curves representing the

²³ Gibson and W. Heitler, *Z. Physik*, 1928, 49, 465.

experimental observations. It is clear that the three calculated curves are widely separated, even if considerable errors were made in the calculations; this is still more the case for the curves (b) in which allowance is made for C_2 in equilibrium with C.

The lowest values for the vapour pressure, *i.e.*, the highest values for the heat of evaporation were obtained by the measurements of vaporisation rates by Wertenstein and Jedrzejewski and Marshall and Norton.⁴ Since this method always gives too low values, it can be understood that the experimental vapour pressure was found only between 1 per cent. (Wertenstein and Jedrzejewski) and 10 per cent. (Marshall and Norton) of the values calculated with $L_C = 168.8$ kcal., whereas the disagreement with the other curves is more than 4 powers of 10.

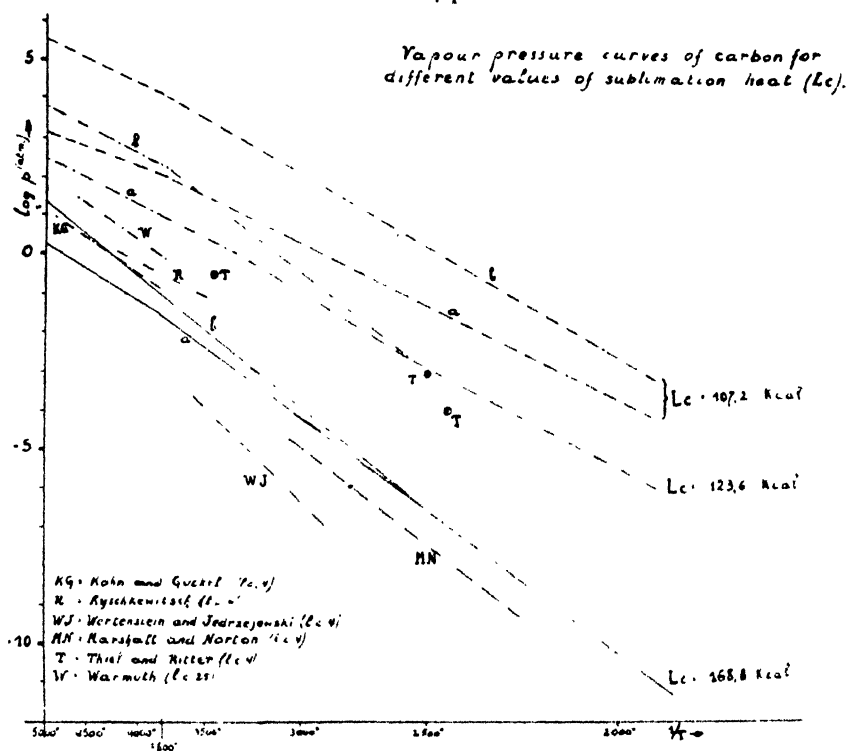


FIG. 1.

On the other hand, we have to consider the fraction of C_2 in the carbon vapour. The corresponding curves in the figure are marked with a "b." In the case of $L_C = 168.8$ kcal. we obtain with the equilibrium constants of Table III. the figures given in Table IV.

TABLE IV.—PARTIAL PRESSURE OF C_2 AND TOTAL VAPOUR PRESSURE OF CARBON CALCULATED FOR $L_0 = 168.8$ KCAL. AND $D_{O_2} = 125$ KCAL.

	T° K.	2000	2500	3000	3500	4000	4500	5000
$\log_{10} P_2$	(atm.)	-12.45	-7.75	-4.6	-2.4	-0.8	+0.35	+1.3
$\log_{10} P$	Total.	-10.38	-6.64	-4.07	-1.92	-0.65	+0.44	+1.37

As can be seen in the figure, this gives a sufficiently good agreement with Kohn and Guckel and Ryschkewitsch' measurements with the arc method.

We arrive thus at the curious result that direct experimental evidence favours the vapour pressure curve which we have to reject on spectroscopic grounds. As a matter of fact, Thiel and Ritter's measurements, although the authors do not claim a high degree of precision, seem to be more in favour of $L_C = 123.6$ kcal. (see the figure), and it is always much easier to understand that equilibrium pressure has not been obtained, than the existence of a pressure which is higher than equilibrium. Furthermore, according to K. Warmuth,²⁴ Kohn and Guckel's temperature values were too high, *i.e.*, their vapour pressure values too low, and this would equally favour $L_C = 123.6$ kcal.²⁵ However, even if we take these points into account, this curve lies very high, and it seems necessary to assume that the vapour pressure of monatomic carbon is practically equal to the total pressure, at least in the lower temperature range, say up to about 2500 or 3000° K. This is only possible for $D_{C_2} \sim 4$ v.c.; curve (b) for $L_C = 123.6$ and 107.2 kcal. has been calculated with this value. Even in this case the vapour pressure reaches a value of 1 mm. at about 2500° and of 1 atmosphere near 3100° K. This is an order of magnitude by several powers of 10 higher than any value hitherto accepted, and it seemed interesting to undertake vapour pressure measurements with a new direct method, especially since the present calculations show that it is sufficient to determine the order of magnitude in order to decide between the different curves and thus obtain an extremely precise value; we hope to publish soon the results of the new measurements which are now in preparation.

Since $L_C = 123.6$ kcal. gives already unexpectedly high values for the vapour pressure, this is *a fortiori* the case for $L_C = 107.2$ kcal.; in this case, even for so low a value of D_{C_2} as 4 v., carbon vapour would be composed practically of C_2 at all temperatures (curve b). A pressure of 1 mm. would be reached at about 1900° K. and 1 atmosphere near 2500° K. This is about 1000 times higher than for $L_C = 123.6$ kcal.

Therefore, also Schmid and Gerö's¹⁵ value of $D_{CO} = 6.9$ v. ($L_C \sim 78$ kcal.) must be considered highly improbable. These authors assume that the evaporation gives carbon atoms in the 5S state: such an interpretation could be possible for dynamical experiments (rate of evaporation). We have to consider, however, that in equilibrium, for such a low value of L_C , practically all the carbon vapour is diatomic, therefore the energy change ΔE of the evaporation is given by equation (1) that is $\Delta E = L_C$ about 73 kcal. for $D_{CO} = 6.9$ v. It seems very improbable that a vapour pressure of the order of that of silver, should never have been observed in the case of carbon, for example, in highly heated carbon tubes.

Summary.

1. Three values of the heat of vaporisation of carbon $L_0 = 168.8$; 123.6; and 107.2 kcal. are discussed. These values were obtained from three values of the dissociation energy of carbon monoxide which are in agreement with the predissociation limit at 11.06 v. The vapour pressure curves of carbon were calculated for these values. Intermediate values can be ruled out by spectroscopic arguments.

2. The direct measurements of the vapour pressure of carbon described in the literature lie mostly between the curves calculated for $L_C = 168.8$

²⁴ *Wissenschaftl. Veröffentl. des Siemenskonzerns*, 1928, 7, 307; *Chemisches Zentralblatt*, 1928, 2, 1800.

²⁵ The temperature scale of Ryschkewitsch was practically the same as Kohn and Guckels, so that his results should also be corrected.

kcal. and 123.6 kcal.; only the values obtained from the rate of evaporation give lower vapour pressures than higher heats of vaporisation. $L_0 = 168.8$ kcal. gives the best agreement but it cannot be accepted for spectroscopic reasons. The vapour pressure calculated from $L_0 = 107.2$ kcal. or still smaller values, is by several powers of 10 higher than can be expected from available empirical data.

3. The most probable value of the heat of vaporisation of carbon is therefore $L_0 = 123.6 \pm 0.5$ kcal. The corresponding value for the dissociation energy of carbon monoxide is $D_{CO} = 9.10 \pm 0.005$ v. = 209.9 kcal. The dissociation energy of C_2 is probably of the order of $D_{C_2} \sim 4$ v. ~ 90 kcal.

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THE ACTION OF ULTRASONIC WAVES IN SUSPENSIONS.

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In a recent paper¹ the formation of stationary wave patterns (Kundt's dust figures in liquids) in emulsions and suspensions caused by ultrasonic waves has been discussed.

A number of other phenomena observed in colloidal or semi-colloidal systems exposed to ultrasonics were found to be connected with this general effect. They are:

- (1) The orientation of anisometric (*i.e.*, rod or plate-shaped) particles in an ultrasonic field.
- (2) The solidification of concentrated suspensions (rheopectic solidification by sound).
- (3) The neutralisation of dilatancy by an ultrasonic field.

A characteristic feature of all systems which exhibit these phenomena is that the particles are big enough to be influenced individually by the sound waves, contrary to the behaviour of normal gels (*e.g.*, iron oxide or gelatin gels), where the disperse system behaves like a continuous homogeneous system of which the particles are so small that energy cannot be scattered by them to any appreciable extent.²

I. Orientation by Ultrasonics.

When investigating the formation of stationary wave patterns in a field of ultrasonics¹ it was natural to expect that non-spherical particles might be orientated with their longer axis normal to the flux of energy.

¹ K. Söllner and C. Bondy, *Trans. Faraday Soc.*, 1936, **32**, 616.

² H. Freundlich and K. Söllner, *ibid.*, 966.

This was tested by applying a field of moderate energy to rather dilute suspensions prepared from rod- or plate-like particles and using suitable containers. Macroscopic pieces of glass or quartz wool and also small plates of mica and mosaic gold which were lying flat in a horizontal tube prior to irradiation, are orientating themselves by assuming a position normal towards the flux of energy (this being parallel with the axis of the tube) as soon as not too weak a field is applied, in this way forming stationary wave patterns.

It is advisable in this experiment and all following ones to secure an electric charge of the particles by adding a suitable electrolyte, generally $\text{NH}_4 \cdot \text{OH}$, otherwise coagulation may become a source of trouble. Furthermore it is here advisable to use partially degassed water.¹

Suspensions of rather fine asbestos fibres possessing only a slight tendency to settle, show the same phenomena when irradiated in a long vertical test- or U-shaped-tube, the particles first being orientated and later on accumulated in the liquid.

An orientation is also indicated by the appearance of a silky gloss in the zones of accumulation of the sediments in horizontal tubes when irradiating similar suspensions containing particles too small to be seen individually. According to the nature and size of the particles the phenomenon may persist (in the sediment) for some time after the irradiation has been discontinued.

With very small energies an impressive demonstration of the orientation phenomenon can be given by using highly dilute suspensions (e.g., of mica, whose particles are too small to settle even in a considerable length of time). It was found most suitable to use long U-shaped tubes (height 20-40 cm., inner diameter 2-5 mm.) held in an upright position. The observations are made in transmitted light. Brilliantly glittering zones at more or less regular half-wave distances appear immediately the specimens are held in the oil. The vibration there is hardly perceptible, the energy being only 20 to 30 mA.

With such low energies no accumulation in any reasonably short period takes place. One notices further that accumulation as found at higher energies persists for some time after the irradiation has ceased, but that orientation of these small particles disappears at once.

The strongest glittering always appears to be at the antinodes. The glittering zones of orientation show a slight incessantly fluctuating motion, because of the somewhat irregular energy transmission, which tends to displace the meniscus. Simultaneously with this the zones of orientation are displaced. They do not disappear, as do the accumulations (formed at higher energies), when the meniscus is displaced.

Individual particles can be seen glittering at one spot for a considerable time, thus proving that the orientation is brought about directly by the sound waves and not indirectly by some kind of streaming or vortex motion in the liquid.

Orientation is in no way linked up with cavitation. This was also confirmed for accumulation.¹ Both effects are equally well produced *in vacuo* and when increased external pressure is applied. *In vacuo* the bubbling and boiling of the liquid must of course be avoided by lowering the energy, otherwise the phenomenon cannot be observed well.

No glittering on irradiation is found with systems containing spherical particles such as emulsions of nitrobenzene or benzene or suspensions of specially prepared glass spheres. After some time of irradiation at low energies, but more rapidly with higher energies, accumulation can be seen, but never any glittering. The difference is so striking that the occurrence of the glittering phenomenon cannot be misjudged.

Other circumstances being equal, bigger particles in suspension are more readily orientated than smaller ones. The same holds in respect of their accumulation.¹ Here quartz powders of definite particle size may be used, quartz powder being another substance easy to orientate by

ultrasonics. Three U-shaped tubes containing quartz powder suspensions with particles from 4 to 10μ diameter, 1 to 4μ , and smaller than 1μ respectively, were irradiated with medium energy: the 4 to 10μ suspensions showed at once distinct glittering; subsequently the $1-4\mu$ suspensions followed showing a weaker effect, finally came the finest suspension, the effect here being still weaker and not increasing, even after many seconds. It became distinct only when the energy was increased.

Mica is the substance most suitable for demonstrating orientation. A suspension containing thin plates of a few μ and less maximal diameter and only so few in number that a turbidity can just be perceived, shows an excellent effect when irradiated with moderate energy.

Other substances, gypsum, steatite, selenite, mosaic gold and quartz powder as mentioned above (diameters up to 20μ) show distinct orientation at moderate energy. Similar behaviour is shown by clay with a particle size of several μ and below, by kaolin ("Stockalite"), whose particles are mainly below 1μ ; and by colloidal graphite in water ("Aquadag," E. G. Acheson Ltd.). In these cases, especially in the last, the orientation is seen at higher energies not only in transmitted but also in reflected light.

Orientation has so far been found in two typical colloidal solutions, viz.: V_2O_5 and Fe_2O_3 . Rather concentrated (about 1.2 per cent.) V_2O_5 -sols, of high "viscosity," containing particles up to 10 and 15μ length were used. (Owing to their extreme thinness these particles can only be seen in the ultramicroscope.) Filled into a U-shaped tube and irradiated with not too low an energy these sols slowly take on a silk-like appearance, the streaks—in conformity with the orientation of the particles—adjusting themselves perpendicular to the axis of the tube. After a minute or so the phenomenon is very pronounced, persisting for many hours or even days, due to the gel-like state of this sol.³ On close observation one sees that the particles are orientated directly and not by some kind of streaming of the liquid; for bigger particles or flakes contained in the sol remain motionless during irradiation.

When diluted four times the same sol shows the orientation—which can only be seen in reflected light—much more quickly, due to its greater fluidity. Regular half-wave structure appears. This is due to the fact that orientation is better developed in the antinodes than in the nodes (see above). In one (diluted) sol only, containing very big ($10-15\mu$) particles, was a very slight accumulation occasionally observed. On diluting the original V_2O_5 -sol fifty or one hundred times, nothing can be seen in reflected light; transmitted polarised light however reveals a distinct orientation.

Similar results were obtained with a very dilute Fe_2O_3 -sol, many years old, whose particles were ultramicroscopic in all three dimensions.

Though the whole matter still needs fuller investigation, one may now state that, with suitable substances, orientation can be obtained much more readily and with less energy than accumulation; also particles which are too small for accumulation may still become orientated. This is easily understood, because in order to obtain any appreciable accumulation, particles must be moved about several tenths of a millimeter, whereas orientation is effected by simply turning the particles into the favourable position, the maximum movement necessary being only of an order comparable with the length of the particles.⁴

Such orientation could perhaps be utilised for manipulating the interior

³ Orientation is particularly strong in sols which tend to form tactoids. (For literature on tactoids, cf., e.g., H. Freundlich, *Kapillarchemie*, Vol. II., 1932, pp. 54 ff.) Thus it seems worth while to investigate, whether there exists an influence of ultrasonics upon the formation of tactoids.

⁴ The formation of non-spherical aggregates during the coagulation of smoke as described by O. Brandt and E. Hiedemann (*Trans. Faraday Soc.*, 1936, **32**, 1101) may be partially caused by a similar orientation effect in gaseous systems.

of closed systems (e.g., living cells) without using any mechanical devices, which might be obnoxious.

II. Rheopectic Solidification Caused by Ultrasonics.

The time of solidification of certain types of thixotropic systems is shortened by submitting them to a more or less regular movement, such as tapping the test-tube containing the sol or slowly rolling it to and fro between the palms of the hands. This phenomenon was called rheoexy.⁵ Rheopectic solidification seems to have a relationship to coagulation produced by stirring.

After it had been found that irradiation with ultrasonic waves may also cause rheopectic solidification⁶ it seemed worth while to investigate the latter phenomenon more closely, particularly in order to see whether it is connected with the local accumulations caused by stationary waves in suspensions¹ and with the orientation of non-spherical particles described above.

At first we studied suspensions of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Their particles ranged at first from about 1 to 10μ ; later owing to their solubility they grew to from 10 - 30μ ; this did not alter their behaviour appreciably. Specimens of gypsum suspensions in distilled H_2O were prepared and sampled in test-tubes of 1.2 cm. diameter which were later sealed, the concentrations of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ranging from 20 per cent. up to 30 per cent.; sedimentation of the suspensions becomes conspicuous after standing for about an hour. Rheopectic solidification could be produced by subjecting the samples to a weak ultrasonic field for a few seconds. Several minutes or hours are required for spontaneous solidification. The lowest concentration for which the effect can be observed is 23 per cent.; below this the gypsum particles are only accumulated forming stationary wave patterns.

On close inspection it was seen that the samples containing the higher concentrated suspensions also show accumulation.⁷

The behaviour of a sample of kaolin ("Stockalite" above-mentioned) was similar. Its particles are anisometric, because a dilute suspension shows the orientation phenomenon; aqueous suspensions containing as much as 60 per cent. solid matter are quite liquid. These suspensions are very poor as regards plasticity and thixotropy. By addition of NaCl solution the charge of the particles is however lowered and Stockalite, thus partly coagulated, forms thixotropic and rheopectic suspensions. For example, 5 g. Stockalite + 8 c.c. 2N NaCl solution remained liquid for at least 17 minutes in a test-tube; on prolonged standing sedimentation can be observed. Upon tapping this suspension solidifies after 30 seconds; in an ultrasonic field of moderate energy (70 mA) only 15 seconds are required. When irradiating for a longer time zones of accumulation are gradually forming in the paste, preferably in narrow tubes.

⁵ H. Freundlich and F. Juliusburger, *Trans. Faraday Soc.*, 1935, **31**, 920.

⁶ F. Juliusburger and A. Pirquet, *Trans. Faraday Soc.*, 1936, **32**, 445.

⁷ We also tested, whether or not the rheopectic solidification by ultrasonics is due to cavitation (cf. C. Bondy and K. Söllner, *Trans. Faraday Soc.*, 1935, **31**, 835 and ⁸). Both under gas pressure and *in vacuo* (bubbling and boiling must of course be carefully avoided) solidification occurs as usual—therefore cavitation need not be considered here. On the other hand rheopectic pastes and gels can of course be disrupted and liquefied when ultrasonics of higher energy are applied. In this respect they do not differ at all from normal thixotropic gels.⁸ The only difference is that, at moderate energies where the effects of cavitation are negligible, systems with very small particles (e.g., thixotropic iron oxide) are not influenced appreciably, whereas systems with larger particles, big enough to be moved individually by the sound waves, may be solidified.

While with the gypsum or Stockalite suspensions the rôle of orientation of the particles cannot be excluded, in addition to the obviously effective accumulation, the latter is certainly solely responsible in the next system, showing rheopexy when irradiated.

Suspensions or sludges of Solnhofen slate^a are rheopeptic, when in a suitable concentration. They also are solidified when irradiated with ultrasound. A temperature of about 35° C. proved favourable. Medium energy (75 mA) was sufficient to solidify the sample in about 3 seconds while the spontaneous solidification occurs in about 30 seconds. The particles of Solnhofen slate do not deviate much from a cubical shape; they, also, do not show an orientation effect. Therefore, in this case at least, rheopexy is possible without orientation, the accumulation of the discharged particles being most likely the only cause of their becoming a paste.

Plastic clay, as used for moulding purposes, shows rheopexy when in suitable concentrations, upon tapping or rolling the test-tube containing the sample to and fro. Its particles are anisometric, for dilute suspensions show the orientation phenomenon. The particles are several μ in diameter and less, and show a weak (but distinct) tendency to form zones of accumulation when irradiated in dilute suspension.

It has however, so far, been impossible to detect a shortening of the time of solidification under various conditions of concentration and electrolyte present. These suspensions show hardly any tendency to settle down; however, in the more dilute ones, some supernatant liquid can be seen after very long standing.

The tendency to form stiff gels—as distinct from the rather soft pastes mentioned above—is obviously also the reason why rheopeptic solidification with ultrasonics cannot be observed. The individual particles are bound so firmly to one another that the whole system behaves as a coherent, more or less homogeneous, gel.^a For this reason zones of accumulation have never been observed in concentrated systems of this kind, which, of course, are formed here too by big foreign particles.^a

We can now also understand why rheopeptic solidification due to ultrasonics has so far not been observed in V_2O_5 -sols (containing suitable electrolytes). These sols scarcely form any zones of accumulation when irradiated. Moreover, the particles, while readily orientated in dilute solutions, are much more slowly orientated in concentrated ones. The interaction between the particles is obviously so strong, that accumulation and even orientation by sound waves is rendered impossible.

These experiments lead to the conclusion that, generally speaking, rheopexy is not necessarily linked up with orientation and that a solidifying influence of ultrasonics is to be expected in those rheopeptic systems, which are more paste- than gel-like and whose particles are big enough to be influenced—by being either orientated or moved—individually by the sound waves.

III. Neutralisation of Dilatancy by Ultrasonics.

If the supernatant liquid is poured off the sediments of various suspensions such as quartz powder or sea-sand, the sediments are somewhat moist and soft, when only a slight pressure is applied. As soon as however a stronger, one-sided, pressure is acting, a sediment of this kind becomes dry and hard and offers considerable resistance to a penetrating instrument; as soon as the pressure ceases the whole mass

^a On the thixotropy and plasticity of Solnhofen slate, *cf.*, Freundlich and F. Juliusburger, *Trans. Faraday Soc.*, 1934, **30**, 333.

^a H. Freundlich and K. Söllner, *ibid.*, 1936, **32**, 966.

usually becomes moist again. This phenomenon called "dilatancy" was explained by Osborne-Reynolds,¹⁰ in the following way: In moist sand the particles tend to assume a very close-packing. If an external force displaces the particles the packing becomes looser and consequently water is sucked in, thus leaving the sediment apparently dry and hard.

When a system normally exhibiting dilatancy is exposed to ultrasonics dilatancy disappears so long as a sufficiently strong field is in action: *e.g.*, a beaker was filled with some quartz sand ("silver sand") and water was added so that the system showed dilatancy. It was not possible to drive a test tube through the sand to the bottom of the vessel. This however was quite easy as soon as a strong ultrasonic field was applied, exposing the beaker to the oil fountain.

A very similar experiment can be carried out using fine quartz powder instead of the sand. In this case more energy is necessary, because owing to the increased scattering surface formed by the much smaller particles the resistance to the sound waves is increased.

In a further experiment, a sediment of quartz sand was freed carefully from all supernatant and adhering water after standing for quite a long time. Its appearance was very dry. When irradiated for several seconds it gave off about 0.5 to 1.0 c.c. water per 100 c.c. sediment. After this water was poured away the sand offered a very great resistance to a penetrating test-tube from the very start. This experiment shows that the sand under the influence of the ultrasonics assumes a packing closer than after being left undisturbed for quite a long time or after being tapped frequently in order to promote settling. Applying a rather high energy (135 mA) it is possible to destroy dilatancy in a beaker containing 2 kg. silver sand mixed with the necessary amount of water.

Here we see how apparently dilatant and, therefore, non-plastic systems, can be rendered somewhat plastic by applying ultrasonics. It can readily be shown that cavitation is not connected with the influence of ultrasonics on dilatancy.

Summary.

(1) With ultrasonics rod- or plate-like particles (mica, mosaic gold, gypsum, selenite, steatite, quartz, kaolin, etc.) can be orientated with their longest axis normal to the flux of energy. To produce this effect the energy may be below the limit necessary for accumulation. These results are obtained as a rule with particles of microscopic size, but orientation was also found in truly colloidal solutions of V_2O_5 and Fe_2O_3 .

(2) Concentrated rheopectic suspensions of gypsum, kaolin and Solnhofen slate are solidified by ultrasonics of low and medium energy. The solidification is correlated to the accumulation of the particles by ultrasonics. If the energy applied is sufficiently high, these concentrated pastes also can be liquefied, as a consequence of cavitation.

(3) Mixtures of sea-sand or quartz-powder with water which are normally dilatant lose this property, when exposed to ultrasonic waves.

Our sincerest thanks are due to Professor H. Freundlich for his continuous interest and very helpful criticism during our work. We are also greatly indebted to Professor F. G. Donnan, F.R.S., for his generous hospitality.

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¹⁰ Osborne Reynolds, *Phil. Mag.*, (5), 1885, 20, 469; *Nature*, 1886, 33, 429.

THE ETCHING OF COPPER BY OXYGEN.

By C. F. ELAM (Mrs. G. H. TIPPER).

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Part I.

Metals heated *in vacuo* frequently etch, *i.e.*, the structure is revealed by partial volatilisation or other surface changes. A very beautiful example is shown in a photograph of pure silver in Rosenhain's *Introduction to Physical Metallurgy*. This photograph not only shows crystal boundaries, but also a series of lamellæ in certain crystals which change direction at crystal and twin boundaries and very much resemble slip-bands in appearance. Such a structure can also be produced on copper when a specimen is heated *in vacuo* at 900-950° C. Figs. 1-6, Plate I, are representative photo micrographs. It will be seen that some crystals are quite free from lamellæ. In others, the lamellæ are straight, while in others again they are curved to a considerable extent. The spacing also varies from crystal to crystal. The iridescent nature of the reflection of light by this etched surface is very striking and, as in the case of pearlite in steel, the cause is similar. In view of the recent interest in the internal structure of crystals, it was decided to investigate the nature of these lamellæ further in order to see what relation they bore to the crystal, if there were any regularity in spacing and further, if they changed in character with different copper and with different treatments.

The first step was to prepare copper crystals large enough for X-ray measurements on which two or more faces could be ground in order to determine the planes (if any) made by the lamellæ themselves. Large copper crystals can easily be made by Bridgman's method using graphite tubes in which to melt the copper, but these crystals did not etch on heating *in vacuo*. Working and annealing the copper failed to produce any effect and the conclusion was come to that the copper was at fault. Other samples of copper available heated in the same tube, at the same time etched, so that the question naturally arose as to why the copper melted in graphite tubes did not. At this stage I applied to the British

TABLE I.

	AJK, Per Cent.	ARQ, Per Cent.	CJR, Per Cent.
Bi	0.0001 or less	0.003	Trace
Pb	0.0005 or less	0.002	Trace
Fe	0.005 approx.	0.005 approx.	0.005 less than
Ni	0.0005 or less	0.01	0.0005 less than
Ag	0.002	0.003	0.0015-0.002
Sn	Not detected	0.01 approx.	0.0005 less than
Mg	Probably of order of 0.01	Trace	Negligible trace
As	Not detected	Not detected	Not detected.
Sb			
Si			

PLATE I.

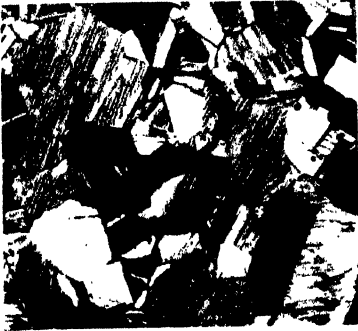


FIG. 1. $\times 150$

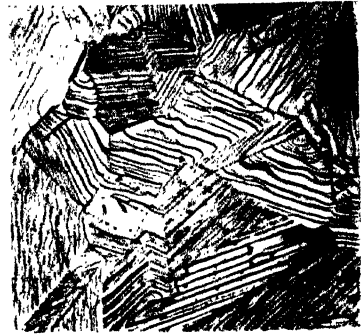


FIG. 2. $\times 400$

Polycrystalline copper from Dr. Alkins.

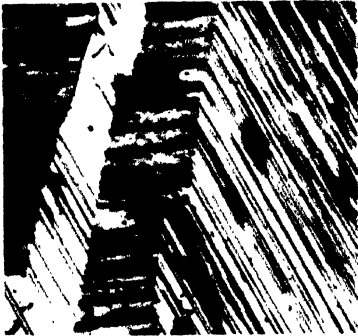


FIG. 3. $\times 150$

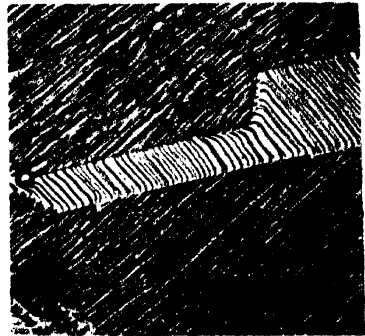


FIG. 4. $\times 400$

Dr. Alkins' copper treated to produce large crystals.



FIG. 5.—A, B and C. $\times 100$

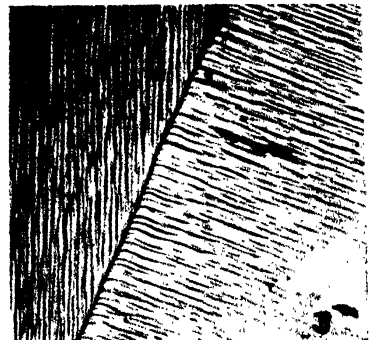


FIG. 6.—A and B. $\times 500$

[See page 1604.

PLATE II.

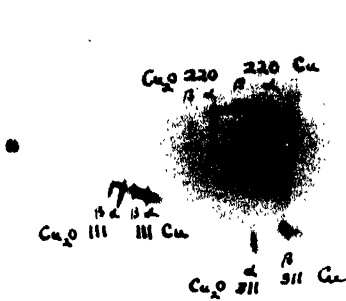


FIG. 8. G_3 with thin layer of oxide, Face 1.

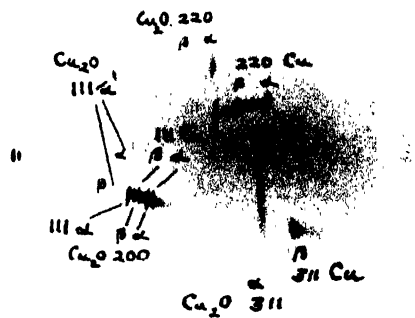


FIG. 9. G_3 , thicker oxide layer, Face 3.

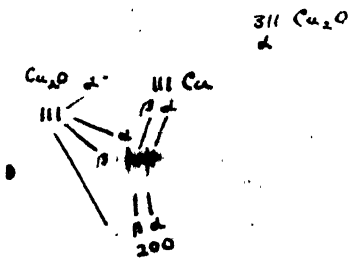


FIG. 10. G_3 same as Fig. 8, Face 2.

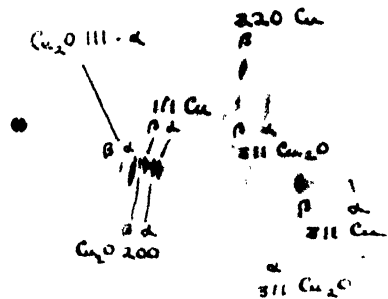


FIG. 11. B coated oxide.

An iron anticathode was used, $K_\alpha = 1.93$, $K_\beta = 1.75$

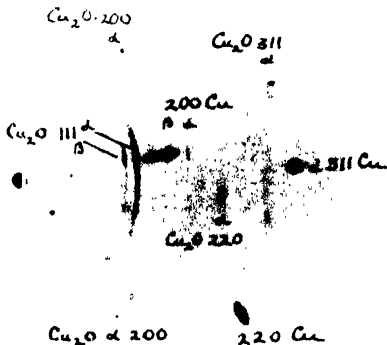


FIG. 13.— G_1 , first oxidation.

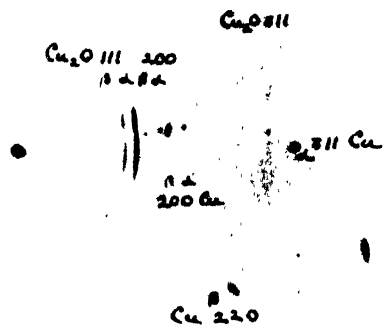


FIG. 14.— G_1 heated 950°C . for 1 hour after oxidising.

[See page 1614]

Non-Ferrous Metals Research Association for samples of copper, one of which was to be the purest available and oxygen-free, and they very kindly supplied me with three different coppers and their spectrographic analyses. AJK and ARQ were cast ingots. AJK was a sample of high conductivity oxygen-free copper; ARQ was a small wire bar of tough-pitch fire refined copper. CJR was cathode copper straight from the cathode.

These coppers were all very pure and only ARQ contained any cuprous oxide. Pieces were cut from them and samples from AJK and ARQ were rolled and then annealed *in vacuo*. Heating was carried out in an alundum boat in a fused silica tube having a ground glass joint to make the necessary connections with the pump. The pump was a Hyvac, which if kept running continuously, gave a vacuum of less than 0.5 mm. pressure. Gases were given out by the metal and tube on heating and if the pump were shut off the pressure sometimes rose 2-3 mm. Of three coppers referred to above, the only specimens that etched were those cut from ARQ.

At this stage the presence of cuprous oxide was suspected of being responsible, and experiments were carried out accordingly. It was noticed that all the coppers that etched contained visible amounts of cuprous oxide. Although the rods from which large copper crystals were made contained a certain amount of oxide, the crystals grown from them, whether melting was carried out in air or nitrogen, contained only traces. What remained was confined to a few minute isolated inclusions at the crystal boundaries. If then, this effect is due to the presence of oxide, treatment removing the oxide should prevent its occurrence. Samples of a number of coppers including ARQ and AJK were heated in a stream of hydrogen at 900° C. for five hours. Those containing cuprous oxide cracked badly under this treatment, but AJK and a piece of a large crystal remained sound. On subsequent heating *in vacuo*, none of them etched. The next step was to add oxide to a copper such as AJK. Certain difficulties were here met with. If melting was carried out in graphite tubes and even a large excess of cuprous oxide rolled up in copper foil added, only traces of oxide remained in the copper. If the same procedure was carried out in alundum crucibles the oxide attacked the crucible and everything went through the pot. Finally, the copper was melted and the oxide added and the metal cooled quickly. This method was successful in introducing the oxide but the crystals in the small ingot—about 60 gms.—were consequently small. Specimens cut from such an ingot etched with ease, and thus provided striking confirmation of the necessity for the presence of oxide. It was also noticed that with repeated heatings, the tendency to etch decreased and finally disappeared with corresponding loss of cuprous oxide. This suggested diffusion of oxygen through the copper crystals and in order to test this further the following experiments were made. A plug of the copper made from AJK containing cuprous oxide was put into a piece of AJK as received, and the two heated in contact for 5 hours at 900° C. The polished surface showed the cuprous oxide in the plug had gone, and the surrounding AJK was pitted but not etched. A section cut and polished showed a core of the plug containing oxide, a narrow rim in which the oxide had disappeared, and a halo effect in AJK was obtained on etching with ammonia which spread outwards on subsequent heating. Similarly, a piece of a bar produced by melting in a graphite tube and showing three large crystals in section, was put as a plug into a sample of ARQ, a section cut and polished and heated at 900° C. *in vacuo* for five hours. The crystals in the plug now etched as well as the surrounding copper. Finally a section of this was cut and polished and heated a second time and this also showed a faint etch.

These experiments, although only qualitative in character, seem sufficient to warrant the assertion that the presence of cuprous oxide is the prime cause of the etching observed. The alundum boat became pink

and also the inside of the silica tube, particularly round the region just inside the furnace. After prolonged heating the boat became white again. Slade and Farrow¹ state that cuprous oxide can be volatilised and this was confirmed by heating some freshly precipitated and dried Cu_2O in the silica tube at 900°C ., when the oxide left the boat and collected round the cooler part of the tube. This is contrary to the findings of Rhines and Mathewson² who, although they found loss of Cu_2O on heating *in vacuo*, say that the oxide was reduced and decomposed. Tiede and Birnbrauer³ noticed a liberation at 960°C . of a red substance, which they assumed to be copper, on heating copper *in vacuo*. Copper did not come off with any freedom till 1360°C . and it is possible that their first evolution was Cu_2O .

Further experiments were then carried out to see if the same effect could be produced by oxidising the surface and then volatilising off the layer of Cu_2O . Oxidation was affected by opening a tap when the metal was hot and letting in a little air. If this was done with the tube withdrawn (the metal itself remained hot in a vacuum long after the tube was out of the furnace) the bright surface of the copper was seen to dull. If the copper was still about 750°C . and a very small amount of air let in, the surface tarnished over and then brightened again immediately. As more air entered the coating of oxide persisted and if the specimens were allowed to cool it appeared black. If the tube was then evacuated and heated at 900 – 950°C ., the coating was distinctly red, i.e., Cu_2O . The outline of the original crystals was clearly indicated in the oxide. After further heating *in vacuo*, varying from 1 to 20 hours according to the thickness of the oxide layer, the whole of the layer disappeared leaving the copper bright and beautifully etched.

As a further check on the results described above, Dr. W. E. Alkins was instrumental in obtaining some special silver-free copper and a further oxygen-free-copper carefully prepared to avoid contamination with oxygen. The silver-free copper contained about 0.016 per cent. oxygen and etched very slightly on heating. By allowing a slight artificial oxidation of the surface it etched as well as any other copper. The specially prepared oxygen-free copper on the other hand did not etch.

It is now possible to speculate a little about the possible causes of this etching effect. It has been shown conclusively that the presence of cuprous oxide in the copper or a layer of oxide on the surface is necessary.

If two samples, one of which etches and the other does not, are heated together in the tube, the one that etches does not effect the other, but if the two are in intimate contact, then the copper which does not etch tends to do so. It seems justifiable to conclude that oxygen diffuses through the copper and on arrival at the surface forms a layer of cuprous oxide which at the correct temperature and pressure volatilises. Recent estimations⁴ of the solubility of oxygen in copper are as follows:—

600° C.	oxygen per cent.	0.0071
800° C.	" "	0.0094
950° C.	" "	0.0100

Although low, it is sufficient for the purpose, the supply of oxygen inside the specimen being provided by the cuprous oxide, which gradually disappears. The fact that the same effect can be reproduced artificially by oxidising the surface and then volatilising off the oxide suggests that this is a rough outline of what actually happens. The details of the process and the relative importance of temperature and pressure and oxide concentration are still obscure.

¹ R. E. Slade, F. D. Farrow, *Proc. Roy. Soc., A*, 1912, 87, 524.

² F. N. Rhines, C. H. Mathewson, *Amer. Inst. Min. Met. Eng. Trans. Inst. Metals Div.*, 1934, 337.

³ E. Tiede, E. Birnbrauer, *Z. anorg. Chem.*, 1914, 87, 129.

⁴ F. N. Rhines, C. H. Mathewson, *Amer. Inst. Min. Met. Eng. Trans.*, 1934, p. 337.

In order to obtain some quantitative measurements of this phenomenon, a piece of oxygen-free copper AJK, $7.58 \times 7.05 \times 16.31$ mm., was heated *in vacuo* at 950° C. twice and the weights compared. Constant weight was obtained. The specimen was then heated and oxidised, the air pumped off and further heated until the copper was bright again, cooled and weighed. The tube had a red coating inside in the cooler region. The figures are given in Table II. This process was repeated. In the

TABLE II.

Treatment.	Weight of Copper.
	Gms.
After 1st heat at 950° C. for 3 hours . . .	7.420
After 2nd heat at 950° C. for 4 hours . . .	7.420
Heated to 950° C., air let in . . .	—
Heated <i>in vacuo</i> at 950° C. till oxide on surface had gone. Oxide still on under side. Tube had red deposit . . .	7.420
Heated 10 hours <i>in vacuo</i> at 950° C. . .	7.419
Heated to 900° C.; air let in; heated $\frac{1}{2}$ hour; then black. Heated 1 hour <i>in vacuo</i> ; then red . . .	7.421 (Increase in weight 0.002)
Heated $3\frac{1}{2}$ hours <i>in vacuo</i> at 900° C. Red gone on specimen; tube coated red . . .	7.420
Heated <i>in vacuo</i> $2\frac{1}{2}$ hours at 920° C. . .	7.419
Heated 14 hours at 950° C. <i>in vacuo</i> . . .	7.417 (Loss of weight 0.002)
Heated in hydrogen at 900° C. for 1 hour. Total heating and cooling period $5\frac{1}{2}$ hours . . .	7.417 (No further loss).
Colorimetric estimation of copper in Cu_2O on tube . . .	0.0022

second experiment the specimen was weighed with the oxide coating. The increase in weight does not necessarily represent the total amount of oxidation as some of the oxide was probably lost immediately the air was pumped off. An approximate calculation of the thickness of the oxide layer gave it as 0.5 mm. assuming that the oxide was uniform over the whole area of surface. The specimen was then heated until it was bright. A slight red stain remained on the alundum boat and the inside of the silica tube was red. There was a distinct loss of weight of the copper and cuprous oxide was found on the inside of the tube. The quantitative relations between loss of weight and amount of oxide on the tube are not likely to be accurate but this experiment provides conclusive proof that cuprous oxide is volatile. It may be suggested that the oxide is decomposed and reformed on the tube, but this is unlikely as the unoxidised copper was shown to be not volatile at 950° C.

The fact that there is no further loss of weight on heating in hydrogen shows that the oxide had all come off in the vacuum heating. The discrepancy between loss of weight and amount of copper found on the tube may be accounted for by the fact that some oxide adhering to the tube from previous heatings was included in the analysis. The tube becomes permanently red after repeated use due to attack of the silica by the oxide.

It is possible that this method of removing oxide from copper might be made use of in the detection and estimation of cuprous oxide in copper. The present experiments are not sufficiently complete to say how far the method might be made applicable to all coppers because loss of weight alone might be due to the presence of volatile substances such as sulphur.

Part II.

In order to make a full investigation of the striations it was necessary to work with copper crystals sufficiently large to enable more than one

face to be examined. At first, no striations could be obtained on large crystals made from the melt, so it was decided to grow crystals by the straining method in rod and strip. The objection to crystals produced in this manner is that they are always twinned and determination of the crystal axes by means of X-rays becomes more difficult. On the other hand when two or more sets of twins are present, determination of the crystal axes can be made by measurement of the traces of the twin bands on two sections at right angles. It is well known that the twin planes of copper are octahedral planes, hence the position of any two such planes is all that is required.

For this purpose some $\frac{1}{8}$ -inch diameter copper rods were obtained through the kindness of Dr. Alkins from Thomas Bolton & Sons. These were cut from a high conductivity wire bar and contained a considerable amount of visible oxide. Crystals 2 cms. long and occupying the whole cross section were obtained, but, as has been said, they showed twinning. These crystals were compared with those made from the melt and treated as described in Part I. and no difference was observed.

In order to find the relation of the striations to the crystal structure, measurements were made of the angle between them and one edge of the face under observation or a scratch on the surface. Determination of the crystal axes by means of X-rays or measurement of the traces of twin planes were also made and the two series of measurements compared. Striations were obtained on two or sometimes three faces ground on the same crystal, but this was not always possible if the crystals were small. This entailed polishing several faces of a specimen before heating so as to be quite sure that all faces were subjected to the same conditions at the same time.

It was usual to find only one set of lines on each face, but there were cases of two appearing. Sometimes the lines were curved and wavy and could not be measured accurately. It is easy to see how such curved lines can arise. Suppose the lines represent traces of planes in the crystal which are nearly parallel with the face of the specimen. Then, any irregularities of the surface would cut the crystal planes in an irregular manner.

The spacing of the lines varied from crystal to crystal as Figs. 1-6, Plate I., show. This again may depend on the angle which the plane makes with the face.

If the planes are of the same indices the distance between them is the same, d , and the distance between successive traces on the surface is $d \csc \alpha$, if α is the angle between the plane and the surface.

Actual measurements of the number of the striations to the millimetre, for example, were abandoned owing to the irregularity of spacing, but it is quite clear that, taking the crystal as a whole, spacing is characteristic of each grain. Absence of striations may indicate that the plane coincides with the face of the specimen or is at right angles to it.

Repeated treatments of one face always resulted in the same set of striations appearing and parallel faces cut on one crystal gave similar measurements. Separate specimens cut from the same crystal also showed the same striations on comparable faces. It seemed, therefore, that they must be related to the copper crystal.

In order to depict the combined results, stereographic diagrams were made of the crystal and positions of the striations marked. If these are related to the copper crystal and represent traces of a single plane, the pole of the plane would be expected to coincide with that of a possible crystal plane in the copper. Assuming that this was the case the pole of a plane which would cut the faces of the specimen in the directions observed, was marked on the stereographic diagram of each crystal and in only one instance did it agree with a likely crystal plane. If, however, the striations represent traces of different planes on different faces, no such relationship will exist. Moreover, if three faces were cut at right angles to each other and treated, confirmation was obtained of the fact that these were purely

surface markings, in that traces observed on the third face did not agree with any possible plane through both the other traces. This is not surprising, since we know that the marks are caused by oxidation of the surface and each face will probably act independently.

Reference to Fig. 7 will make these points clear, and a summary of results with other crystals is given in Table III.

It has been assumed that only important crystal planes need be considered. The agreement between striations and traces of possible planes was good, and it does not seem to be necessary to give actual measurements in each case. Where the striations marked on the diagrams coincided with the pole of an important crystal plane, *i.e.*, (110) for example, more

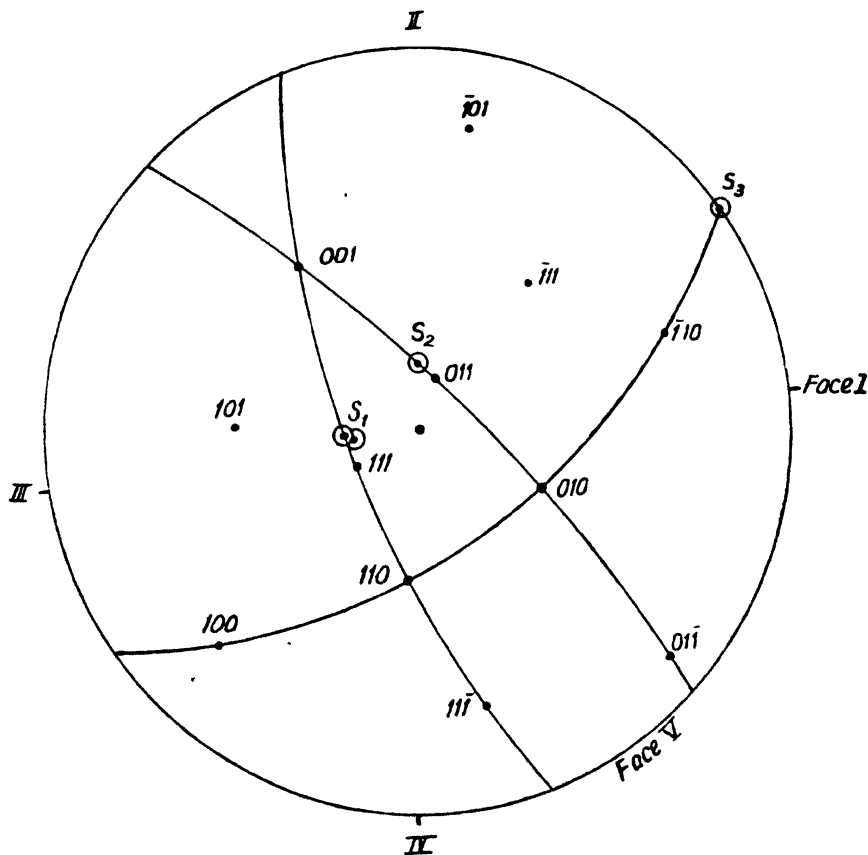


FIG. 7.— G_2 .

$S_1 = (\bar{1}10)$, $S_2 = (100)$, $S_3 = (001)$.

than one interpretation was possible, as several possible planes pass through this point. The (111) planes must be included but only one case was met with in which a (111) plane was the *only* possible plane.

From Table I. it appears that most of the striations are possible traces of (100) or (110) planes, and that it is rarely the same plane on two faces. The question naturally arises what relationship do these planes bear to the surface? Assuming that the striations have been correctly attributed to the crystal planes, a very wide variation is met with, and there is no obvious connection between angle of plane to the surface and formation of striations. In order to be quite sure on this point a comparison was made between the striations on the surface of the main crystal and its

twin bands. Knowing the form of twinning in copper, it is possible to calculate the position of the planes in each twin band. This was done for two faces of one crystal, and the results are given in Table IV. In this

TABLE III.

Description of Copper.	Crystal Planes whose Traces Coincide with Striations.		
	Face I.	Face II.	Other Faces.
Strip $\frac{1}{4}$ -inch	(100)	(001)	—
Alkins rod :			
0	($\bar{1}01$)	(111) ?	—
1	(100)	(100)	—
2	(100) or ($0\bar{1}1$)	(101) or ($\bar{1}11$)	—
3	(100)	(100)	—
4	(010)	(001)	—
Melted in graphite tube :			
A	(001), ($1\bar{1}0$) or ($1\bar{1}1$)	} Only one face available	
B	(101)		
C	Nil		
Made from AJK with Cu_2O added :			
D	(01 $\bar{1}$)	Two Sets. (101) and (100)	
E	(10 $\bar{1}$)	(100)	
F	($1\bar{1}0$) or (001)	Two Sets. ($11\bar{1}$) or (101) and (001)	
Large crystal made in graphite tube :			
G_1	(001)	(100)	Face III.
G_2	($\bar{1}10$)	($\bar{1}10$) or ($\bar{1}\bar{1}1$)	72° to Face I. 90° to Face II.
—	Faces I. and III.	Faces II. and IV.	(100), ($\bar{1}\bar{1}1$) or ($0\bar{1}1$) Faces V. 90° to Faces I., II., III. and IV.
G_3	($\bar{1}10$)	(100) nearly same as II. in G_1	(001) Same as I. in G_1

TABLE IV.

	Striations.			
	Face I.		Face II.	
	Plane.	Angle Between Face and Plane.	Plane.	Angle Between Plane and Face.
Main crystal	(101) or ($\bar{1}11$)	68° or 22°	(100) or ($0\bar{1}1$)	78° or 13°
Twin (111)	(100)	36°	(010)	32°
Twin ($\bar{1}11$)	(100)	57°	twin not present.	
Twin (11 $\bar{1}$)	twin not present		Nil.	
Twin (1 $\bar{1}1$)	(110)	83°	(001)	8°

case there can be no difference in composition which could affect the result and the angles between the planes and the surface are very different. There appeared to be no reason why bands corresponding to the twin on the (111) plane showed no markings on Face II. This twin did not appear on Face I.

Special reference is necessary to three crystals in one specimen A, B and C, a photograph of which is shown in Figs. 5 and 6, Plate I. The striations on A and B were repeated in the same position every time the specimen was heated, but C had only a few faint markings. Comparing the orientation of the three crystals relative to the surface, it was found that in C, a {100} plane was perpendicular to the surface. If we assume that the striations are due to preferential attack by oxygen along certain planes—just as occurs by attack in solutions—the ends of all these planes being inclined at an angle to the surface, appear dark with vertical illumination. It is justifiable to assume that the "ends" are also crystal planes, also of type {100} or {110} planes. In crystal C, any attack along the (001) plane, would be perpendicular to the surface and no "step" would appear. It is probable, however, that the crystal being symmetrical to the surface, the attack may have been along a number of possible directions with the result that no one direction predominated and the surface remained smooth.

It is interesting to note that etching reagents attack copper crystals along directions corresponding to {100} and {110} planes.⁵

Part III.

In order to try to account for the formation of the striations along certain planes in preference to others, an investigation was made of the structure of the oxide layer in its relation to the copper crystal. The specimen was polished and heated to the required temperature *in vacuo* and a few cubic centimetres of air let in. One experiment was made of letting in air before heating was begun. In some cases heating was continued in presence of air; in others the air was immediately pumped off and heating continued. It was generally found necessary to do this in order to insure that all the oxide was in the form of Cu_2O .

The structure of cuprous oxide⁶ has been determined by means of X-rays and is face-centred cubic, the side of the elementary cube being 4.25 Å. Each oxygen atom has four copper atoms arranged round it tetrahedrally.

It is difficult to estimate the thickness of the oxide layer but it was probably of the order of 0.1 to 0.5 mm.* X-ray photographs always showed reflections from the copper crystals underneath in addition to those of the oxide. All the reflections from the oxide agreed with the theoretical structure of cuprous oxide with the dimensions given above. Instead of the well-defined spots obtained from single crystals, the reflections were often more in the nature of parts of rings, but showed marked concentration of intensity at certain points. This type of photograph is characteristic of those obtained from a number of small crystals showing preferred orientation along certain directions, *i.e.*, a "Fibre-structure." A typical photograph is shown in Fig. 8, Plate II. This illustrates the difference between the reflections from the copper crystal and those from the oxide. It also shows quite clearly that the arrangement of the oxide is related to the copper. Copper has a face-centred cubic structure in which $a = 3.61$ Å. If the spacings for copper and the oxide are compared it will be found that in certain cases, *e.g.*, {311} planes in oxide and {220} plane of copper, they are very close but in others there is no agreement. Consequently it is unlikely that parallel growth in the true sense will take

⁵ G. Tammann, *J. Inst. Metals*, 1930, 44, 29.

⁶ M. C. Neuberger, *Z. Krist.*, 1931, 77, 169.

* See p. 1607.

oxide is still differently orientated. Reference to a stereographic projection of a cubic crystal shows that the pole of the (001) plane (for example) lies in the (110) plane and is $54^{\circ} 44'$ from the (111) and ($\bar{1}\bar{1}\bar{1}$) planes respectively. In order to replace the (001) plane by the (111) plane it is necessary to rotate the (110) plane $54^{\circ} 44'$ about its normal. At the same time the (001) plane replaces the ($\bar{1}\bar{1}\bar{1}$) plane. By this process we arrive at the structure found in the cuprous oxide and if this interpretation is correct a [110] direction should be common to both copper and oxide. In the case of crystal G, Fig. 12, this direction is the normal to the (110) plane in the diagram. Most of the oxide is thus arranged in two ways: (1) the orientation is nearly the same as the copper crystal; (2) a rotation of $54^{\circ} 44'$ has taken place about a [110] direction. This structure is again typical of a fibre structure. Most of the reflections can be referred to one or other of the orientations given above, but a concentration of parts of {111} rings perpendicular to and at 55° - 60° to the face indicates that some of the crystals are rotated through other angles about the [110] direction.

The oxide layers on crystals A, B and C and G₁, ₂ and ₃ were fully investigated and all showed the same kind of structure. The degree of preferred orientation seemed to depend on the condition of the surface of the copper. The first coating of oxide showed less preferred orientation than a second deposited after the first layer had been volatilised off, even if the metal had been heated for some time at 900° C. before oxidising. The characteristic appearance may be compared in Fig. 14 and Figs. 8-11, Plate II.

Bircumshaw and Preston have also found by the electron diffraction method a preferred orientation of Cu₂O on poly-crystalline copper, a {111} plane being parallel to the polished surface.⁷

The oxide crystals were so small that no individual spots were visible but after prolonged heating at 950° C. growth occurred as Fig. 14, Plate II. shows. It was also found that after heating at this temperature faint rings appeared on the X-ray film corresponding to pure copper indicating that some of the oxide had decomposed leaving small copper crystals on the surface. In most cases, repeated oxidation gave an oxide layer orientated in the same way, but in crystal C, different results were obtained.

The results show that the first layer follows the orientation of the copper closely, but that subsequent layers differ progressively. It is suggested that the outermost layers give rise to those reflections which do not fit either of the two principal orientations and approximate to a random arrangement.

Discussion of Results.

The experiments just described are sufficient to warrant the assumption that the beautiful etching effect in copper and probably silver* is due to an oxidation of the surface and subsequent volatilisation of the oxide in a high vacuum. Attack by solvents along certain planes in preference to others is a common occurrence and the regularity in the striations suggests a periodicity in the structure of the crystal. But the photographs show that the distance between successive striations is by no means constant although the average width of the bands is characteristic of each crystal. It was also noticed that there was very little difference between all the coppers examined and these had a variety of treatments. The most important cause of variation was the preparation of the surface and this is a difficulty that is not easily avoided. Even prolonged heating at 950° C. did not remove the effects of polishing. It is suggested that all mechanical methods of preparing a surface are

* A few preliminary experiments have failed to obtain the etch effect in silver which was very pure and had been vacuum annealed.

⁷ G. D. Preston, L. L. Bircumshaw, *Phil. Mag.*, 7, 1935, 20, 706.

likely to vitiate the results of the study of surface phenomena. The marked difference observed in the character of the X-ray reflections, whether the spots are well-defined; the presence of Debye rings, etc., is attributed to the perfection or otherwise of the surface.

It is well known that one substance will crystallise on another so that the orientation of both is the same if the two are isomorphous. In the present instance both substances are cubic although the lattice structure and dimensions are not identical. A certain degree of resemblance in orientation is to be expected but complete agreement is unlikely, and this is actually what is found. It is hoped that a full explanation of the formation of the oxide layer and the reason for the choice of orientation will be obtained and that this may throw some light on the preferential attack of the copper crystal by oxygen.

Summary.

It is shown that an etching effect obtained on heating copper *in vacuo*, is due to the presence of cuprous oxide. The effect can be produced artificially by oxidising the surface and it is suggested that the etch is due to attack by oxygen along crystal planes similar to the action of any etching agent. The planes most readily attacked appear to be [100] and [110] planes of the copper crystal.

The relation between the orientation of the copper crystal and the cuprous oxide formed when copper is oxidised in the presence of a small quantity of air at low pressures was investigated. The first layer to be formed consists of small crystals arranged approximately in the same way as the copper. Subsequent layers take the form of a fibre structure in which a [110] direction agrees closely with the first layer and with a [110] of the copper crystal.

I wish to thank the Leverhulme Research Fellowship Committee for a grant in aid of this investigation. Professor C. E. Inglis, F.R.S., has very kindly allowed me to work in the Engineering Department of the University, and I am also indebted to Professor R. S. Hutton for special facilities in the Goldsmiths Metallurgical Laboratory, and to Dr. D. Stockdale for help on several occasions.

THE SUBOXIDES AND SUBHALIDES OF CADMIUM.

By R. E. HEDGER AND H. TERREY.

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In this work an attempt was made to prepare the subhalide by solution of cadmium in molten cadmium chloride and the suboxide by decomposition of the so-called subhalide by water. The products obtained were examined by means of their X-ray spectra. The analytical results agreed with those of Morse and Jones,¹ but the structures found were identical with those given by (1) the normal chloride and (2) normal oxide and metal. This is in harmony with results obtained by other physical measurements on the solid products, e.g., density, heats

¹ *Amer. Chem. J.*, 1890, 12, 488.

of solution, magnetic properties, etc., and it must be concluded that subhalides and suboxide are incapable of existence as solid phases.

Experimental.—Thermal analysis of the system Cd, CdCl₂.

To carefully purified cadmium chloride rendered anhydrous in a stream of HCl gas increasing amounts of cadmium were added and the melting points of the resulting mixtures determined, a calibrated thermocouple being used. The melting was carried out in a fireclay crucible with a luted lid—a slow stream of CO₂ being passed through an aperture in the lid to prevent oxidation. The addition of cadmium was continued until the maximum depression of the melting-point was obtained. At the end of each determination samples were removed from the mass for analysis, which was carried out by a determination of the chlorine content. The results are tabulated above.

M. Pt.	Chlorine Content.		Mol. Per Cent. of Cadmium.
568°	---		0
558°	37.9	37.8	3.4
544°	36.8	36.9	7.7
530°	35.6	35.5	12.5

These results are in good agreement with those of Aten. The maximum

depression 12.5 mol. per cent. of cadmium corresponds to the Morse and Jones compound Cd₄Cl₇. With greater cadmium content the mass separates into two phases—the saturated solutions of Cd in CdCl₂ and CdCl₂ in Cd.

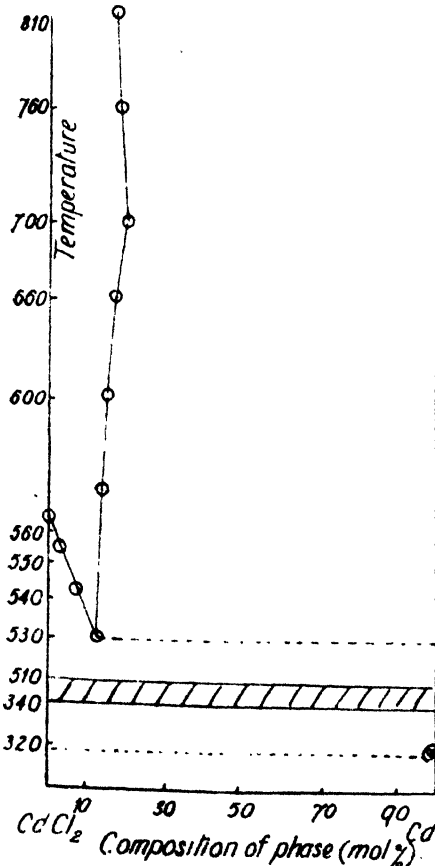


FIG. 1.

Solubility of CdCl₂ in Cd.

This was determined by adding cadmium chloride to cadmium and finding the melting-point and composition of the mass. It was found only possible to dissolve 0.2 mols. per cent. of the chloride in the metal which lowered the melting-point from 322° C (M.Pt. of pure cadmium to 319° C. The two sets of results are shown graphically in Fig. 1.

Investigation of the System Cd-CdCl₂ at higher temperatures.

The experimental procedure in this case was to heat equal mixtures of cadmium and cadmium chloride in a sealed silica tube in an electric furnace to the required temperature. The tube was periodically shaken to ensure equilibrium being set up. At the end of the heating the tube was dropped into cold water in order that the solidified layers should have the same composition as when liquid. The two layers were separated, a clear division being obtained with ease, and each analysed.

The results are summarised in Table I. and also shown graphically in Fig. 1.

TABLE I.—CADMIUM CHLORIDE—
CADMIUM PHASE.

Temperature.	Per Cent. of Cl.	Mol. Per Cent. of Cd.
570	35.3	13.6
610	34.9	15.1
660	34.4	17.0
700	33.4	20.6
760	33.85	18.7
810	34.1	18.1

The figures below agree with those of Aten² up to his maximum temperature 633°. The discontinuity in the solubility is difficult of explanation. A similar effect was noted by Eggink³ in the system Bi, BiCl₃ and there ascribed to the formation of a lower chloride. We were at first inclined to favour this view here. One, however, might reasonably expect that in the rapidly quenched mass some indications of the existence of a subchloride would be found. X-ray photographs of the mass from specimens above and below the point of discontinuity gave line spectra

identical with that of the normal chloride. Although the photographs given by the quenched mass were hazy and not suitable for reproduction there was no difficulty in measuring the position of the lines and the thirty-two recorded agreed well within the experimental error with those of CdCl₂. It is interesting to note that cadmium lines did not appear on these photographs, the metal being disseminated throughout the mass in a very finely divided state.

Increase in temperature had little effect on the solubility of cadmium chloride in cadmium, the chlorine content varying between 0.12-0.16 per cent. corresponding to a cadmium mol. per cent. content of 99.8-99.75.

Cadmium subhydroxide and suboxide.

The eutectic mixture—the so-called compound Cd₂Cl₃, was taken and washed repeatedly with water for 2 to 3 days until the washings were free from chlorine ions. The resulting mass which was of a dark grey colour was dried in a vacuum desiccator and analysed. Found: Cd 86.0, 86.1. Cd (OH) requires 86.9.

The above substance was then heated in a paraffin bath at 300°, a stream of dried nitrogen freed from oxygen by treatment with heated copper turnings being passed over the heated material. A dark yellow powder with all the reducing properties attributed to it by Morse and Jones was obtained. Analysis gave cadmium contents of 92.9 and 93.0 per cent., Cd₂O requires 93.3 per cent.

Powder photographs of this mass were taken and compared with the normal oxide. As is evident from these the spacings and intensities of the two are identical and it must be concluded that the so-called suboxide is merely a mixture of the normal oxide and very finely divided metal.

Summary.

An attempt was made to prepare the suboxide and subhalide of cadmium. Although the analytical data agree fairly well with the formulae given to the sub-compounds X-ray photographs of the products do not support this view. Data are given for the solubility of cadmium in cadmium chloride over the temperature range 570-810° C.

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Inorganic and Physical Chemistry,
University College,
London.*

² *Z. physikal. Chem.*, 1910, **73**, 578.

³ *Ibid.*, 1908, **67**, 779

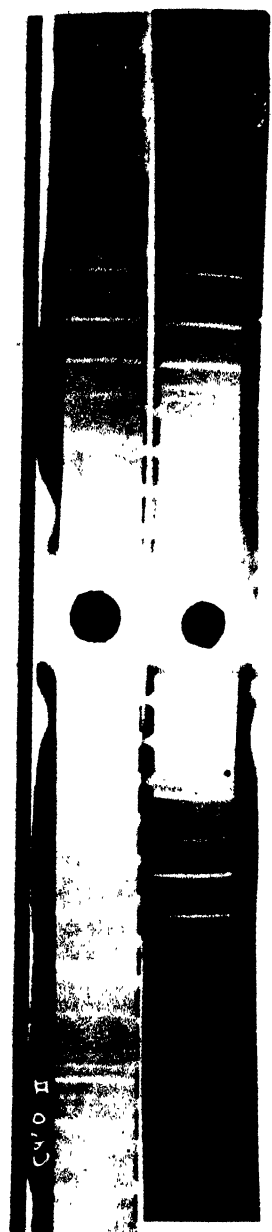


Fig. 2

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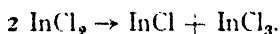
THE PREPARATION AND PROPERTIES OF INDIUM DICHLORIDE.

BY J. K. AIKEN, J. B. HALEY AND H. TERREY.

Received 19th August, 1936.

Although the existence of indium dichloride has never been questioned, it has equally never been satisfactorily proved. The usual preparative methods yield a substance whose composition approximates to InCl_2 but analyses vary considerably; and the reaction with water, the final products of which are metallic indium and the trichloride,¹ is very unusual in a halide. Also, from the position of indium in the Periodic Table the expected chlorides would be InCl and InCl_3 and not InCl_2 as such, although the latter might be considered as a loose molecular associate of the two stable chlorides. The vapour density evidence of Nilson and Pettersson² is inconclusive since the values obtained (at 606°C . obs. 8.15; calc. for InCl_2 7.58) might equally well be produced by mixtures of InCl , InCl_3 and chlorine.

The customary method of preparation, *i.e.* by the action of dry HCl on metallic indium^{1,3} has several disadvantages, *e.g.* if the slightest trace of moisture is present irreversible formation of InCl_3 occurs and, in the presence of oxygen, the oxychloride InOCl is formed. Klemm,⁴ using carefully controlled temperatures and in the presence of carbon dioxide, still found a tendency for the formation of the trichloride even at temperatures as low as 420° , while below 320° the chlorine content was too low (37.14 per cent. obs.; 38.18 per cent. calc.). Klemm⁴ also examined the interaction of the metal and the trichloride as a possible preparative method and concluded that the liquid dissociates to some extent into the mono- and tri-chlorides:—



By the use of a mixture of hydrogen and HCl the presence of any traces of InOCl or InCl_3 can be avoided. It was found that if the trichloride was heated in a stream of hydrogen in an apparatus similar to that used by Mathers⁵ for the preparation of the trichloride, a gradual reduction to the metal took place; the stage $\text{InCl}_3 \rightarrow \text{InCl}_2$ readily and quantitatively at about 600°C (just above the sublimation point of the trichloride) and the stage $\text{InCl}_2 \rightarrow \text{InCl}$ with more difficulty at about 700° . The oxychloride, although only slowly affected by hydrogen alone, is readily attacked by a mixture of hydrogen and HCl .

If the mixture of gases contained rather less than 20 per cent. HCl , and the working temperature did not exceed 600° , the reduction was completely stopped at the dichloride stage. The complete absence of water and oxygen in the HCl (difficult to ensure) is now unnecessary since any formation of InOCl and InCl_3 is precluded. Another advantage of this method is that the starting material need not be metallic indium, but may

¹ A. Thiel, *Z. anorg. Chem.*, 1904, 40, 328.

² Nilson and Pettersson, *Z. physik. Chem.*, 1888, 2, 657.

³ L. de Boisbaudran, *Comptes Rend.*, 1888, 100, 701.

⁴ Klemm, *Z. anorg. Chem.*, 1926, 152, 252.

⁵ Mathers, *J. Am. Chem. Soc.*, 1907, 29, 495.

be the hydroxide or the trichloride, the latter probably being the better. The trichloride was prepared by the method of Mathers³ from $\text{In}(\text{OH})_3$, which had been dried at 100° . The presence of iron chlorides colours the InCl_3 yellow; these can be easily separated by fractional sublimation. The same apparatus was used for the reduction to the dichloride, it being possible to pass in pure dry HCl , hydrogen or nitrogen either together or separately. A slow stream of hydrogen containing about 15 per cent. HCl was passed over the InCl_3 , while the tube was heated to low redness at the constriction. The dichloride collected as a yellow liquid in the second bulb and was gradually distilled along the tube in the same gaseous mixture. It was then heated just above its melting-point in a slow stream of nitrogen for about $\frac{1}{4}$ hour to remove HCl , allowed to cool and sealed off.

The final product was a white glassy solid melting *sharply* to a very pale yellow liquid, which solidified equally sharply. The melting-point, measured in an atmosphere of nitrogen with a micro-thermocouple (copper-constantan in a Pyrex capillary), was $235^\circ \pm 1^\circ \text{C}$ and the boiling-point approximately 570°C . Cl found = 38.07 per cent.; theoretical value, 38.19 per cent. In found = 61.60 per cent.; theoretical value, 61.81 per cent.

In the liquid phase there is some tendency for the dichloride to dissociate into the mono- and tri-chlorides; this dissociation is also produced by the action of water (*cf.* indium dibromide) followed by the decomposition of the monochloride into indium and the trichloride. Indium oxychloride and trichloride are produced by the action of steam, while moist air produces the metal in addition to these compounds. If the dichloride is heated strongly in moist air, InOCl and InCl_3 are first produced, and at higher temperatures the oxychloride decomposes to In_2O_3 and InCl_3 .

A striking feature of the properties of indium dichloride is its strong resemblance in physical properties to anhydrous stannous chloride (first mentioned by Klemm)⁴ *viz.* :—

	Indium Dichloride.	Anhydrous Stannous Chloride.
Appearance.	White glassy solid with a conchoidal fracture.	White glassy solid with a conchoidal fracture.
Specific gravity.	Hygroscopic. 3.64 *	Hygroscopic. 3.90 †
Melting-point.	$235^\circ \text{C}.$ ‡	$246.8^\circ \text{C}.$ *
Liquid.	Pale yellow, darkening with increasing temperature.	Pale yellow, darkening with increasing temperature.
Boiling-point.	<i>ca.</i> 570° .	606° . ⁷
Crystallographic data (see X-ray section).	Orthorhombic. $b_0 = 9.64 \pm 0.06 \text{ \AA}.$ $a : b : c = 0.710 : 1 : 1.093$	Orthorhombic. $b_0 = 9.34 \pm 0.04 \text{ \AA}.$ $a : b : c = 0.708 : 1 : 1.069$

* Klemm⁴ also gives 3.64.

† Klemm gives 3.95.

‡ Klemm gives 235° .

In this connection it is noteworthy that the specific conductivities of the fused substances are unequal; that of stannous chloride being considerably greater than that of indium dichloride.⁶ This similarity gives weight to the supposition that, in the solid state, the dichloride is a definite compound. Since it seemed possible that the two solids might be isomorphous an X-ray examination of the pure chlorides was undertaken.

Preparation of Anhydrous Stannous Chloride.—Commercial SnCl_4 , $2\text{H}_2\text{O}$ was heated in a pyrex distillation apparatus in a stream of dry HCl until frothing ceased. It was then distilled over, collected and redistilled in the same apparatus. The distillate was kept just above its melting-

⁶ Kendall, Crittenden and Miller, *J. Am. Chem. Soc.*, 1923, 45, 963.

⁷ Bilz and Meyer, *Z. physik. Chem.*, 1888, 2, 184.

point, first in dry HCl and then in dry nitrogen and finally poured off and stored in a vacuum desiccator over P_2O_5 .

Density Measurements.—The densities of the solid chlorides were measured in dry nitrobenzene which had been stood over anhydrous sodium sulphate and distilled three times. The mean of several determinations gave 3.90 for stannous chloride and 3.64 for indium dichloride.

X-Ray Technique.—Although crystallographic measurements of anhydrous stannous chloride have been reported by Nordenskjöld⁸ who stated that the crystals belong to the orthorhombic system with $a : b : c = 0.7366 : 1 : 1.068$, many attempts in this present work to obtain satisfactory single crystals have been unsuccessful, *e.g.* (a) by sublimation both above and below the melting-point of the chloride (the former in vacuo); (b) by crystallisation from many solvents such as absolute alcohol, ether, benzene, *o*-dichlorobenzene and thionyl chloride; very small clusters of crystals were obtained from absolute alcohol but it was impossible to separate out any single crystals; (c) by the hot-wire method of Bernal and Crowfoot.⁹ As no direct experimental details of the method employed by Nordenskjöld were available, his method for the preparation of a single crystal could not be attempted and thus the X-ray analyses could only be carried out on powdered samples of the chlorides.

Similarly it was not found possible to obtain single crystals of indium dichloride by any of the above methods.

Experimental.

The specimens were ground in a desiccator over P_2O_5 . During the exposure, the indium dichloride specimens were supported in thin Lithia glass tubes (0.5 mm diameter) which were sealed at both ends. These tubes were used in order to prevent any possibility of the dichloride taking up water during the exposure with its subsequent decomposition.⁴ Again for the same reason the exposures were completed as rapidly as possible by using a small diameter camera; the exposure time being about 20 minutes. This limits the accuracy of the ultimate lattice constants but the photographs were poor and the object of the work is more to show the similarity of the two substances rather than the precision determination of the lattice constants. The stannous chloride specimens were supported in thin collodion tubes (0.5 mm. diam.) and photographed in a larger diameter camera as the danger of decomposition is not nearly so great as with indium dichloride. The glass tubes were found to be unsuitable in this case owing to the production of a very high background density.

Cu $K\alpha$ radiation was used for the final experimental work. Mo radiation was tried in the preliminary experiments and produced clearer photographs but the lines were too close for measurement (even when filtered with zirconium oxide). Fe radiation produced photographs whose density was too great for any measurements to be attempted. In all cases dilution of the specimens with pure dry starch (*cf* Davey)¹⁰ had little or no effect.

Pure, dry sodium chloride was used for calibration purposes and was separated from the main sample by means of a plug of cotton wool.

In all cases the strictest precautions were taken to prevent the entrance of moisture during the grinding and exposures of the samples.

The specimens were oscillated through a 10° arc during the exposures. The values of the reflection angles, in angular measure, were averaged from the separate films (two for indium dichloride and three for stannous chloride).

All the resulting powder photographs were very poor, possessing a high background density making measurement difficult and for these reasons

⁸ Nordenskjöld, *Bihang. K. Sv. Vet-Akad. Handl.*, 1874, 2, no. 2.

⁹ Bernal and Crowfoot, *Trans. Faraday Soc.*, 1933, 29, 1032.

¹⁰ W. P. Davey, *Study of Crystal Structure and its Applications* (New York), 1934, p. 118.

the visual intensities reported in the tables must be treated with caution. It was found possible to measure with certainty 17 lines for indium dichloride and 16 lines for stannous chloride; only those lines whose existence on either side of the centre was in no doubt have been used in the calculations.

The calculated values of d for both the chlorides were found to fit the same logarithmic plot for orthorhombic crystals¹¹ at the approximate axial ratios $a:b:c = 0.71:1:1.1$ from which the indices marked * in tables were obtained. The calculated values of the lattice constants obtained from these indices were utilised to index the remaining planes which could not be indexed directly from the plot owing to its complexity at low values of d .

For orthorhombic crystals the quadratic form for each reflection, assuming zero errors, is:—

$$A_0 \cdot h^2 + B_0 \cdot k^2 + C_0 \cdot l^2 = \sin^2 \theta$$

where: A_0 , B_0 and C_0 are respectively $\lambda^2/4a_0^2$; $\lambda^2/4b_0^2$; $\lambda^2/4c_0^2$.

The observation equations for each reflection were combined, by Gauss's method,¹² yielding three normal equations which were solved, by determinants, for A_0 , B_0 and C_0 †:—

$$A_0 \Sigma h^4 + B_0 \Sigma h^2 k^2 + C_0 \Sigma h^2 l^2 = \Sigma h^2 \sin^2 \theta$$

$$A_0 \Sigma h^2 k^2 + B_0 \Sigma k^4 + C_0 \Sigma k^2 l^2 = \Sigma k^2 \sin^2 \theta$$

$$A_0 \Sigma h^2 l^2 + B_0 \Sigma k^2 l^2 + C_0 \Sigma l^4 = \Sigma l^2 \sin^2 \theta$$

TABLE I.—INDIUM DICHLORIDE.

Mean camera diameter = 57.48 mm. Cu K α = 1.539 Å.

Indices.	Intensity.	θ° .	d_{exp} .	d_{theor} .	$\sin^2 \theta_{exp}$.	$\sin^2 \theta_{theor}$.
*110	vs	7° 59'	5.54 ₁	5.58 ₄	0.0193	0.0190
*020	s	9 8	4.84 ₈	4.82 ₀	0.0252	0.0256
*102	m	10 34	4.19 ₈	4.17 ₈	0.0336	0.0335
*112	m	11 32	3.84 ₉	3.83 ₈	0.0400	0.0399
*200	vs	12 58	3.42 ₉	3.42 ₆	0.0504	0.0505
113	s	14 47	3.01 ₈	2.97 ₄	0.0651	0.0660
220	vs	15 59	2.79 ₈	2.79 ₈	0.0758	0.0761
224	w	23 31	1.92 ₉	1.91 ₇	0.1592	0.1597
330	vw	24 27	1.85 ₉	1.86 ₁	0.1713	0.1711
342	vw	29 5	1.58 ₈	1.57 ₇	0.2362	0.2368
430	s	30 41	1.50 ₈	1.51 ₁	0.2604	0.2595
432	m	32 3	1.45 ₉	1.45 ₈	0.2816	0.2804
532	vw	38 51	1.22 ₇	1.22 ₄	0.3935	0.3940
505	m	42 16	1.14 ₄	1.14 ₉	0.4524	0.4526
615	w	50 18	1.00 ₉	0.99 ₉	0.5920	0.5914
711	w	52 29	0.97 ₉	0.97 ₉	0.6291	0.6301
713	w	55 6	0.93 ₈	0.93 ₈	0.6727	0.6719

Combination of the 17 observation equations using the values of $\sin^2 \theta_{exp}$. and solution of the resulting three normal equations yields the final equation:—

$$0.0126_2 h^2 + 0.0063_7 k^2 + 0.0053_3 l^2 = \sin^2 \theta$$

from which:—

$$a_0 = 6.8_5 \pm 0.04 \text{ Å.} \quad a_0/b_0 = 0.710 \pm 0.012$$

$$b_0 = 9.6_4 \pm 0.06 \text{ Å.}$$

$$c_0 = 10.5_4 \pm 0.06 \text{ Å.} \quad c_0/b_0 = 1.093 \pm 0.008$$

Density for 8 molecules of InCl_2 or 4 molecules of $\text{In}_2\text{Cl}_4 = 3.53$.

Experimental density = 3.64.

¹¹ Fairbanks, *Laboratory Investigation of Ores* (New York, 1928), p. 79.

¹² Mellor, *Higher Mathematics*, p. 557.

† Cf. M. U. Cohen.¹³ The correct form of Cohen's equation, i.e. with the addition of the "drift constant D " was not used as it was considered unnecessary owing to the large experimental error resulting from the poor powder photographs.

¹³ M. U. Cohen, *Rev. Sci. Instr.*, 1935, 6, 68.

TABLE II.—ANHYDROUS STANNOUS CHLORIDE.
Mean camera diameter = 104.95 mm. Cu $K\alpha$ = 1.539 Å.

Indices.	Intensity.	θ° .	$d_{exp.}$	$d_{theor.}$	$\sin^2 \theta_{exp.}$	$\sin^2 \theta_{theor.}$
*110	vs	8° 11'	5.408	5.402	0.0203	0.0204
*102	m	11 3	4.014	3.983	0.0367	0.0373
*112	s	12 8	3.661	3.664	0.0442	0.0441
*022	s	13 1	3.417	3.411	0.0506	0.0509
130	w	15 52	2.815	2.815	0.0747	0.0748
032	s	16 59	2.634	2.641	0.0853	0.0850
203	vs	19 11	2.342	2.344	0.1080	0.1076
230	w	19 59	2.252	2.265	0.1168	0.1155
310	w	21 4	2.141	2.143	0.1292	0.1289
311	m	21 29	2.101	2.095	0.1341	0.1348
224	m	24 53	1.829	1.832	0.1771	0.1763
313	w	25 13	1.806	1.802	0.1815	0.1822
410	w	28 7	1.624	1.626	0.2245	0.2239
342	vw	30 13	1.529	1.525	0.2533	0.2547
423	m	33 7	1.409	1.410	0.2984	0.2976
404	w	33 56	1.379	1.377	0.3116	0.3119

Solution of the three normal equations yields :—

$$0.01357h^2 + 0.0067k^2 + 0.0059l^2 = \sin^2 \theta$$

from which :—

$$\begin{aligned} a_0 &= 6.61 \pm 0.03 \text{ Å.} & a_0/b_0 &= 0.708 \pm 0.009 \\ b_0 &= 9.34 \pm 0.04 \text{ Å.} \\ c_0 &= 9.98 \pm 0.04 \text{ Å.} & c_0/b_0 &= 1.069 \pm 0.006 \end{aligned}$$

Density for 8 molecules of SnCl_2 or 4 molecules of Sn_2Cl_4 = 4.00.
Experimental density = 3.90.

The deviation of the theoretical densities from the experimentally measured values, for both the chlorides, lies within the experimental error of the lattice constant determinations. When comparing the above experimental axial ratios for stannous chloride with those given by Nordenskjöld,¹ it must be remembered that although, in his paper, the figures are stated to be only approximate they are given to 4 decimal places; in addition the author appears to be in doubt as to the purity of his sample.

It should be noted that seven preparations of indium dichloride and five of stannous chloride yielded identical powder diagrams; the latter including a preparation by the action of dry HCl on metallic tin.

The preparation and analysis show that, in the solid state, indium dichloride is a definite chemical entity and this is confirmed by the X-ray evidence. Its very close resemblance to anhydrous stannous chloride shows that it cannot be a "molecular" compound of the residual valency type. That this resemblance to some extent persists in the liquid phase is shown by the similar, but by no means equal, specific conductivities and boiling-points.

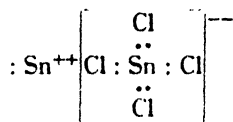
It is now reasonable to assume that the vapour density values of Nilson and Pettersson² are actually due to the presence of associated molecules of In_2Cl_4 , more particularly so since this effect is also observed with stannous chloride.¹⁴ The solids are no doubt completely associated to compounds of the type M_2Cl_4 , as in the case of anhydrous cupric chloride and other anhydrous metallic chlorides. The fact that molecular weight determinations of stannous chloride in organic solvents^{15, 16} indicate that it exists as single molecules cannot be taken

¹⁴ Biltz and Meyer, *Ber.*, 1888, 21, 22.

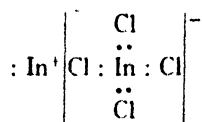
¹⁵ Werner and Schuler, *Z. anorg. Chem.*, 1897, 15, 1.

¹⁶ N. Castoro, *Gazz. Chim. Italiana*, (ii), 1898, 28, 317.

as evidence for the molecular condition of the solid (*cf.* for example molybdenum dichloride, which is trimolecular in the solid¹⁷ although unimolecular in urethane; ¹⁸ the latter being one of the solvents used for the molecular weight determination of anhydrous stannous chloride).¹⁸ Stannous chloride (*cf.* cupric chloride) is probably derived from H_2SnCl_4 with the following structure :

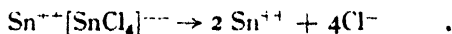


Similarly indium dichloride is probably derived from HInCl_4 :—

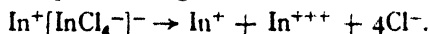


These structures, although differing in ionic charges, have identical electronic configurations, which would lead to strong physical similarities between the two chlorides. The larger ionic charge of anhydrous stannous chloride would also account for its greater conductivity in the fused state.⁴

It may be supposed that these complex ions are relatively unstable, being decomposed by solvents and partly dissociated on fusion (more particularly so on vaporisation). The breakdown of the complex SnCl_4^{--} ion will lead to the formation of Sn^{++} and Cl^- ions, *i.e.* simply ionised SnCl_2 , *viz.* :—



while that of the InCl_4^- ion will give In^+ , In^{+++} and Cl^- ions, *viz.* :—



The above reactions provide a logical explanation of the action of water and heat on indium dichloride. The yellow colour of the fused chlorides can then be explained by the presence of small quantities of stannous chloride (SnCl_2) and indium monochloride respectively. This is supported by the observation that if indium dichloride is heated in a sealed, evacuated tube (*i.e.* under conditions favourable to this dissociation) and suddenly cooled, the solid is coloured yellow or red.

We wish to point out that the suggested structures are based on chemical rather than X-ray evidence.

Summary.

A new method for the preparation and the chief properties of indium dichloride are described.

This substance is shown to be similar in physical properties to anhydrous stannous chloride. X-ray analysis shows both substances to belong to the orthorhombic system with similar lattice constants.

Evidence is presented to support the view that both substances are associated in the solid state.

The Sir William Ramsay Laboratories of Inorganic and Physical Chemistry, University College, London.

¹⁷ Blomstrand, *J. prakt. Chem.*, 1861, **82**, 423.

¹⁸ Ephraim, *Inorganic Chemistry (English Trans.)*, 1934, p. 239.

THE INTERACTION OF CARBON DISULPHIDE AND SULPHUR DIOXIDE.

BY B. CRAWLEY AND R. H. GRIFFITH.

Received 8th September, 1936.

The fact that carbon disulphide reacts with sulphur dioxide, in contact with alumina, to give carbon dioxide and sulphur, has been recorded by Lenander.¹ A survey has now been made of a wide range of catalysts for this reaction.

The apparatus employed is shown in Fig. 1. A stream of sulphur dioxide was measured by the flow gauge A, and passed over carbon disulphide in the saturator B, which was kept at any desired temperature in a thermostat. The mixture then entered the reaction tube made of

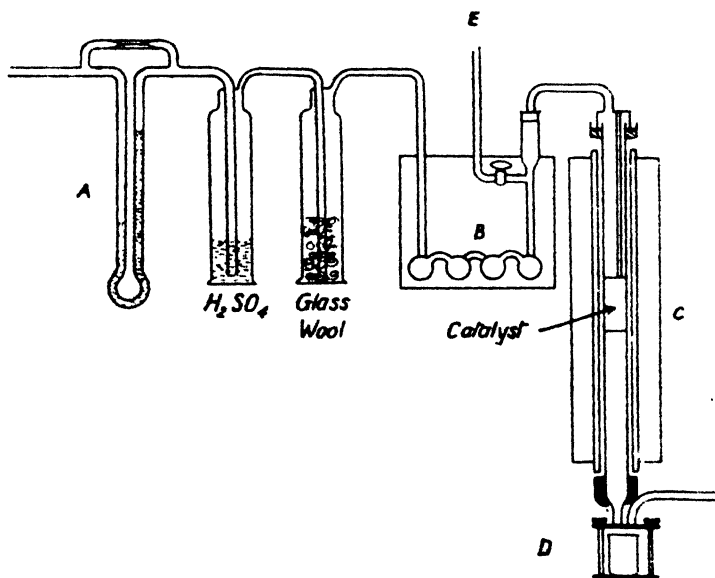


FIG. 1.—Apparatus for catalytic reaction between CS_2 and SO_2 .

Monel metal and heated in the electric furnace C. The lower end of this tube was also heated so that molten sulphur ran out of it into the collector D, which consisted of a glass vessel having a detachable metal head and containing a beaker of convenient size in which the solid product could be weighed. The system was freed from air by means of a stream of nitrogen entering at E. Comparative tests with various catalysts were carried out at 450° and atmospheric pressure by determining the weight of sulphur formed in 1 hour with a rate of 80 c.c. of sulphur dioxide per minute. The results were expressed as the weight of sulphur which would be given by

¹ U.S. Pat. 1,904,482, 1,904,483, *Brit. Chem. Abstr.*, B, 1934, 145.

shown by velocity curves given in Fig. 6. It is clear that Van der Waals' adsorption also takes place simultaneously, but owing to the overlap of the two types it was found impossible to separate one from another.

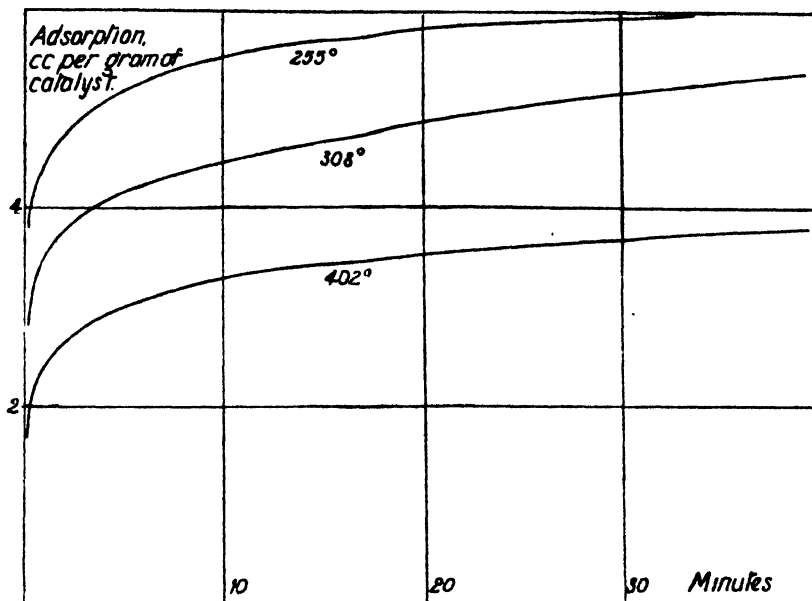


FIG. 6.—Adsorption velocity curves for SO_2 on titanium sulphide.

Discussion.

The feature of particular interest in this reaction is that activated adsorption of only one reactant is shown to be necessary. It is also evident that this type of adsorption first has a measurable velocity at just the same temperature as the reaction is detectable. The change therefore appears to occur by collision of a free carbon disulphide molecule with an adsorbed sulphur dioxide molecule.

It is intended to investigate the kinetics of this reaction more closely.

The facts now presented have also some significance with relation to the hydrogenation of carbon disulphide to give methane and hydrogen sulphide. Titanium sulphide is one of the most active catalysts for this reaction, at 400-450°, and the change therefore occurs similarly by collision of carbon disulphide with adsorbed hydrogen. It has been found that activated adsorption of hydrogen takes place on titanium oxide (unpublished data) and it must be presumed that it occurs equally on the sulphide.

*No. 1 Laboratory,
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THE KINETICS OF SIMULTANEOUS POLYMERISATION AND RING FORMATION.

(A note in reply to Dr. Stoll.)

By. G. SALOMON.

Received 14th August, 1936.

A paper of the author's on this subject¹ occasioned some criticism.² The paper consisted of a survey of research results, without the inclusion of experimental details, and the kinetic analysis, being one in common use, was represented on this occasion only by some simple differential equations. A part of the author's experimental results have now been published in detail³ and in this lengthy publication the points on which misunderstanding had arisen have been clarified.³ They may be briefly summarised :

(1) Dr. Stoll does *not* discuss the constant of a first order reaction but that of a run made at one concentration only ; this is not permissible.⁴

(2) The enhanced reactivity of the imines is not " unsupported by experimental data " but was made very probable by the experimental results, which conform with the differential equations. The " schematic " example is calculated by Stoll with arbitrarily chosen constants, though Ostwald⁵ showed long ago that the position of the turning point depends on the *ratio* of these constants

(3) Conclusions as to uncatalysed and irreversible imine-formation, if deduced from the kinetics of the catalysed, autocatalysed and reversible lactone-formation (esterification), are not possible on account of the difference in dimensions.

(4) In the determinations of yields by Stoll following the progress of the syntheses titrimetrically, water, which participates in the reaction and the presence of which is necessary for catalysis, is discontinuously distilled away.

(5) Determinations of yields in lactone-syntheses were calculated by Stoll with an unproved integral and comparisons carried out with the " constants " so obtained. This is at variance with the axioms and definitions of chemical kinetics. Moreover the arbitrarily established differential equations are applicable not to esterifications but to uncatalysed and irreversible reactions. If, however, the comparison of yields is carried out without the aid of mathematical apparatus, it has been proved, table 24,³ that the polymers isolated *originate in different reaction-courses, four different esterification-reactions being possible*. This result is in good agreement with the researches of Carothers⁶ and the predictions of Ziegler.⁷

¹ *Trans. Faraday Soc.*, 1936, **32**, 154, but in Advance Proof, September 1935.

² M. Stoll, *Trans. Faraday Soc.*, 1936, **32**, 1031 ; M. Stoll and A. Rouvé, *Helv.*, 1935, **18**, 1087 ; *cf.* 1092-1096.

³ G. Salomon, *Helv.*, 1936, **19**, 743.

⁴ Van't Hoff, *Vorlesungen über theoretische und physikalische Chemie*, 2. Auflage, 1. Teil pages 191-192 ; Mellor, *Chem. Statics and Dynamics*, London, 1904.

⁵ Ostwald, *Allgemeine Chemie*, II, 1896, pp. 264-266, *cf.* Fig. 5.

⁶ Carothers, Hill, Van Natta, Spanagel, and others, *Am. Soc.*, 1929-1936 ; *cf. Am. Soc.*, 1936, **58**, 654.

⁷ K. Ziegler, H. Eberle and H. Ohlinger, *Ann.* 1933, **504**, 94-130 ; *cf.* pp. 98, 100.

As often in organic chemistry, such *determination of yields demonstrates only the accessibility*, but not the ease of formation of the compounds isolated. Ziegler whose ingenious pioneering work is built up on purely kinetic considerations has already demonstrated¹ that comparison of yields may be successfully carried out without mathematical apparatus.

Added in proof (13/x/1936): The last paper of the writer² has now been criticised by Dr. Stoll,³ who, however, finds no new experimental data which weaken the arguments outlined above. The author emphasises that the differential equations he used in his earlier papers are identical with those involved in his last paper. Moreover, not the slightest change has been made in the application of Ostwald's method of kinetic analysis.

Note by Editor.—Further notes on this paper¹ will not be published in these *Transactions*.

*The University,
Reading.*

¹ K. Ziegler and R. Aurnhammer, *Ann.*, 1934, **513**, 43-64.

² M. Stoll and A. Rouvé, *Helv.*, 1936, **19**, 1079.

THE RAPID MEASUREMENT OF THE OXIDATION OF INSULATING OILS IN AIR.

BY A. GEMANT.

Received 13th July, 1936.

The author recently investigated¹ the absorption of air by mineral oils for a temperature range of 20° to 80° C. The method used was a manometric one, and it seemed obvious that a similar apparatus could be used for the determination of the tendency of an oil to oxidise at higher temperatures. Although a certain amount of work exists already on the subject of oil oxidation,² the results so far obtained have not been completely conclusive and it was decided to carry out further experiments on this line which are here recorded.

It is generally agreed that the oxidation rate of an oil is not an absolutely reliable measure of its stability in practical service: coking tests, measuring carbon deposits, or sludge tests are generally preferred as laboratory methods. The British Air Ministry makes use of the change in viscosity after a prolonged treatment³ in its test for lubricating oils. Weiss and Vellinger⁴ consider the change of different physico-chemical factors after an artificial ageing much more important than the actual measure of oxygen absorption.

There exist, however, several methods for testing an oil by its actual oxidation rate. Mardles⁵ and Ornstein and collaborators⁶ determine

¹ A. Gemant, *Trans. Faraday Soc.*, 1936, **32**, 694.

² See, for instance, D. R. Pye, *The Internal Combustion Engine*, Oxford, 1934, **2**, 118.

³ F. H. Garner, C. I. Kelly and J. L. Taylor, *World Petroleum Congress*, London, 1933, **2**, 448.

⁴ H. Weiss and E. Vellinger, *ibid.*, 1933, **2**, 423.

⁵ E. W. J. Mardles, *Trans. Faraday Soc.*, 1931, **27**, 681.

⁶ L. S. Ornstein, C. Janssen, C. Krygsman and D. Th. J. ter Horst, *Physica*, 1935, **2**, 201.

the absorbed oxygen by chemical analysis; Evers and Schmidt⁷ by the number of coulombs necessary to replace the loss by electrolytic oxygen, while Evans⁸ makes use of the simple manometric method.

The two chief advantages of the test described below are its simplicity and its quickness, it being possible to complete one in approximately two hours. Although a more prolonged test certainly yields results more in accord with the actual behaviour in service, cases often arise where, for some reason or other, a quick estimation of the quality of the oil is required.

The Method and Apparatus.

If oil is kept in a closed space at a high temperature and constant pressure, the progressing oxidation can be measured by means of a manometer indicating the steadily decreasing volume of the gas above the oil. Such measurements are rather unsuitable for chemical investigations

since the decrease in volume is really the algebraic sum of two terms, the positive terms being given by the volume of oxygen absorbed by the oil and the negative one by the volume of volatile gases formed as a result of the oxidation of the oil. But since our present purpose is only to find some characteristic difference between oils of different quality, it does not matter much whether the results are fit for chemical analysis or not.

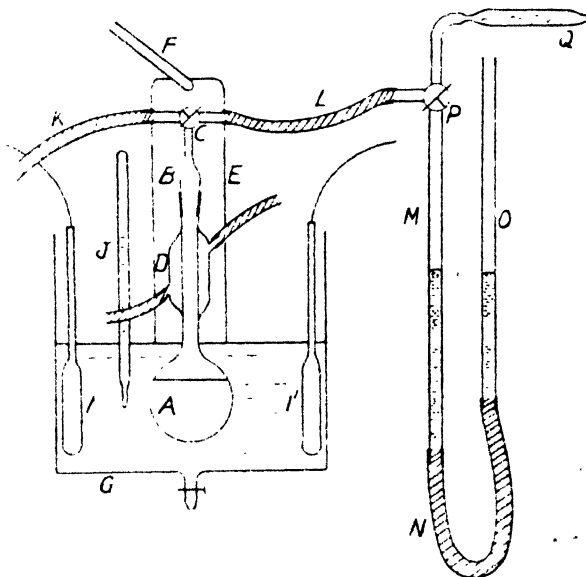


FIG. 1.—Diagram of oxidation apparatus.

In order to obtain quick changes in the volume of the air, the latter was chosen to be of the same order as that of the oil in contact with it, in contradistinction to the arrangement of other experimenters, using a much larger volume of air than of oil. In any case the change in volume cannot be directly interpreted as a rate of oxidation, since the decrease of the concentration of oxygen in the gas phase has to be taken into consideration. In a comparatively short time equilibrium between oil and gas will be reached and the whole process stops. This on the other hand is not a disadvantage, so long as the process itself is really different for oils of differing grade.

The apparatus used is shown diagrammatically in Fig. 1; A is a glass bulb of some 200 c.c. content, filled with 130 c.c. of the oil to be measured. B is a ground-glass joint, leading to the three-way stopcock C. The tube D serves for cooling the upper part by continuously running water, thus

⁷ F. Evers and R. Schmidt, *Erdöl und Teer*, 1933, 9, Nos. 1 and 2.

⁸ E. A. Evans, *World Petrol. Congress*, London, 1933, 2, 460.

keeping the joints tight during heating. The whole was mounted on the board E and shaken, if required, by the arm F of a shaking device. G is an oil bath, with electric heaters I and I' and a thermometer J. The tubing K leads to a pump and the tubing L by means of the stopcock P, to a manometer with two separate branches M and O joined by the tubing N. Q is a calcium chloride tube to keep the system dry.

Readings are taken by shifting the right branch of the manometer, until both are level. The volumes given in the following graphs are always reduced to normal conditions (0° C. and 760 mm. Hg pressure), and to 100 gm. of oil.

Results for Constant Temperature.

The best results can be obtained by keeping the temperature at a certain constant value, and plotting curves relating changes in gas volume to time. In Figs. 2 and 3, the decrease in volume is measured in c.c.,

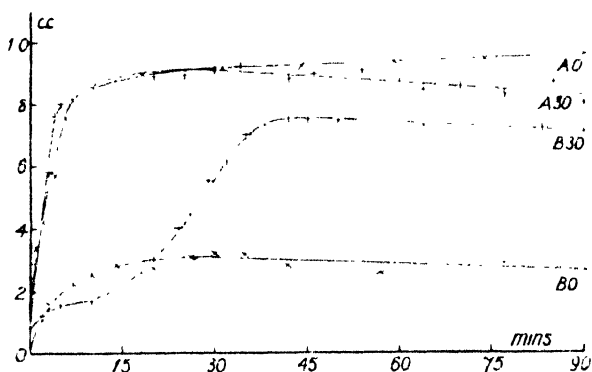


FIG. 2.—Oxidation curves for four oils at 155° C. (reduced c.c. of gas against mins.).

and the time in minutes. Each figure contains data for four special oils at 155° and 145° C. respectively. Copper catalyst was always present.

In this paper only thin oils of the insulating type are considered, but the extension of the method to other oils, for instance lubricating oils, is certainly feasible. A few

data of the four oils (supplied by Messrs. Silvertown Lubricants, Manchester) are summarised in Table I. All these, with the exception of No. 4, are heavily acid refined.

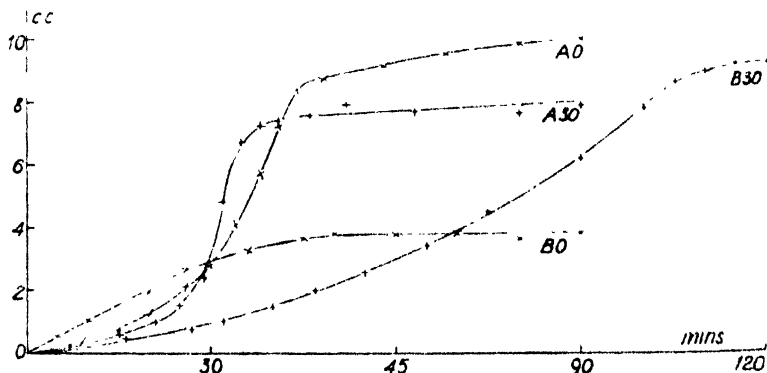


FIG. 3.—Oxidation curves for four oils at 145° C.

In comparing the results for the four different oils, consider first the 155° curves (Fig. 2). A 30 and A 0 show a rapid absorption, which suddenly stops, the change afterwards being a slight decrease for A 30, a slight increase for A 0. B 30 shows rapid absorption first, which is soon

TABLE I.—DATA OF OILS.

Number.	Grade to British Standard Specification.	Origin.	Sludge Fig. per Cent.
1	A 30	Russia	0.02
2	A 0	America : Kansas, Oklohama	0.05
3	B 30	Russia	0.21
4	B 0	America : Eastern Pennsylvania	0.53

replaced by a slower process, finally stopping like the other two. B 0 exhibits only the first rapid absorption which stops very soon, the curve slightly decreasing further.

Although it is not possible to draw definite conclusions without a more detailed work (chemical analysis of the gas), it is still evident that the aspect of the curve is strikingly different for oils of different grade.

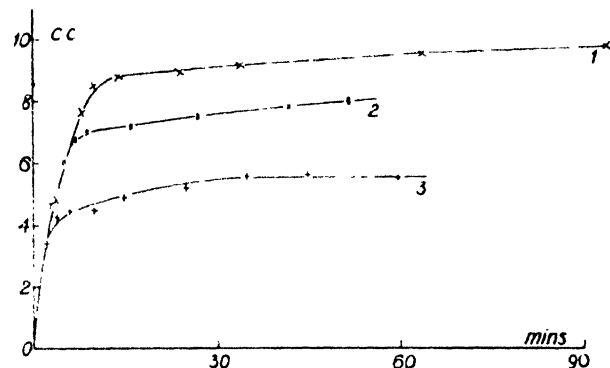


FIG. 4.—Repeated curves for a sample of A 0 oil at 155° C. (in intervals of 3 days).

Summarising the differences we could say that the steeper the curve and the higher the ordinate which it finally reaches, the higher the quality of the

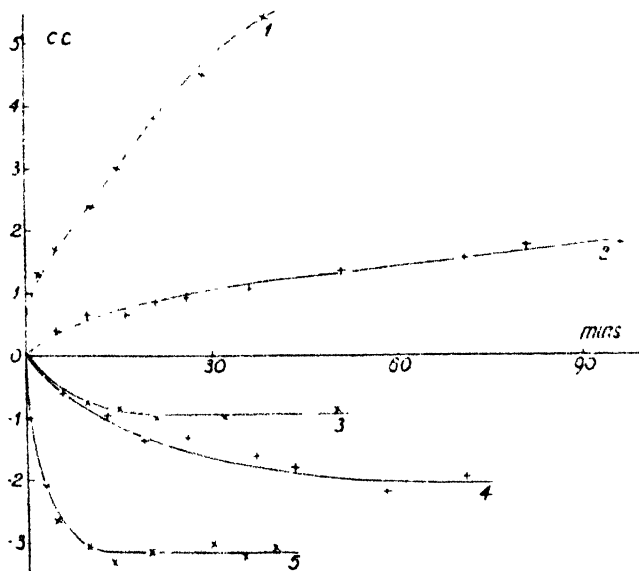


FIG. 5.—Repeated curves for B 0 oil at 145° C.

oil. This somewhat paradoxical result may be accounted for by the fact that the less stable the oil, the further oxidation proceeds and the more likely the formation of volatile, low molecular end products, *e g.*, acids, which counteract the decrease of the gas volume. A gas-analysis after the oxidation is finished, would show whether this assumption is right. Hence the range of the

four oils is : A 0, A 30 (both very nearly the same) ; B 30, B 0 in good agreement with the sludge figures.

The difference between the curves in Fig. 3 (for $145^{\circ}\text{C}.$) still exists on similar lines, although it is somewhat blurred by induction periods exhibited by the A grade oils. It must be remembered (and will be shown later) that the above behaviour for $155^{\circ}\text{C}.$ is reversed at lower temperatures (below $140^{\circ}\text{C}.$), where the volume changes are the more pronounced the less stable the oil, since in this temperature range the curves are controlled mainly by the absorption rate of oxygen. It follows, therefore, that the above striking difference is best exhibited at temperatures very near $150^{\circ}\text{C}.$, since at still higher temperatures (above $160^{\circ}\text{C}.$) the production of volatile products probably dominates the process for any type of oil.

Repeated Measurements with a given Sample.

The above result can be completed by repeating the same process on the same given sample of oil. Fig. 4 shows the result for the A o oil at 155° ; Fig. 5 for the B o oil for $145^{\circ}\text{C}.$, the curves being taken at intervals of 2-3 days. The high-quality oil shows the same type of curve at each repetition, with the final height, however, continuously decreasing. Even in this case volatile products are formed, which slightly increase with

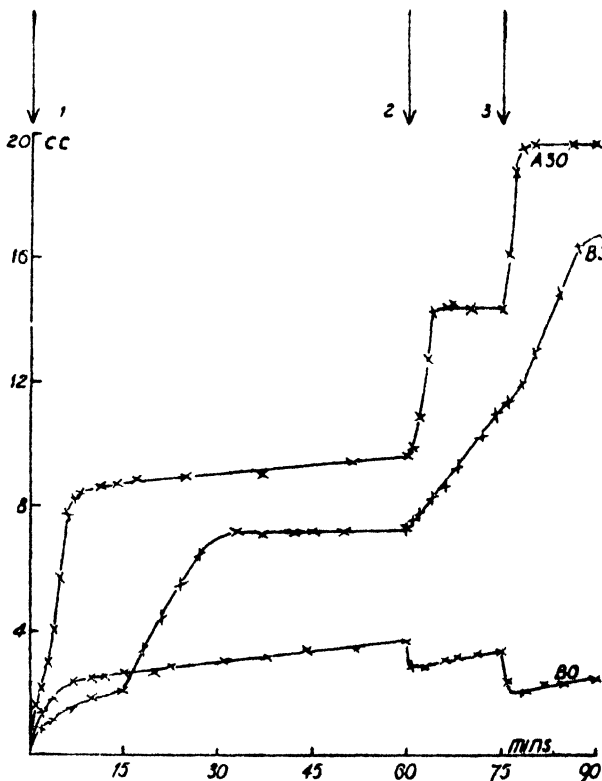


FIG. 6.—Curves of oxidation at $155^{\circ}\text{C}.$ with immediate repetition (at times indicated by arrows).

time. (The first total decrease seems to correspond quantitatively to the amount of oxygen existing in the bulb.)

The B o oil on the other hand yields quite different curves at each repetition (Fig. 5), and clearly, at the third time, one entirely on the negative side, showing a predominance of gaseous oxidation products over the oxygen absorbed.

A rather instructive comparison is shown in Fig. 6, including data for oils Nos. 1, 3 and 4 at $155^{\circ}\text{C}.$ After 60 minutes shaking, the bulb was brought to rest, rapidly exhausted by means of the pump (no change in physical absorption takes place during a few seconds with the oil at rest), and fresh air let in. Then shaking began and after 15 minutes the same procedure was repeated. Whereas the character of each repeated curve remains unchanged, so far as the A oil is concerned, there is a marked drop at the beginning of each new portion in the case of the B o oil.

Curves with Varying Temperature.

Finally, Fig. 7 shows the rate of change of volume plotted against temperature for all four oils. The ordinates are the logarithms of (reduced) c.c. of gas per minute, the abscissæ temperature.

By a reasonable extrapolation of the curves beyond their measured range, it is seen that below say 140° C. the B grade oils lie above the A grade oils, whereas above say, 150° the opposite is the case. A rapid test below 140° is, however, not feasible, since the oxidation rate is generally so low that the change in gas volume would not become obvious enough in a short time. Hence our choice of 155° C.

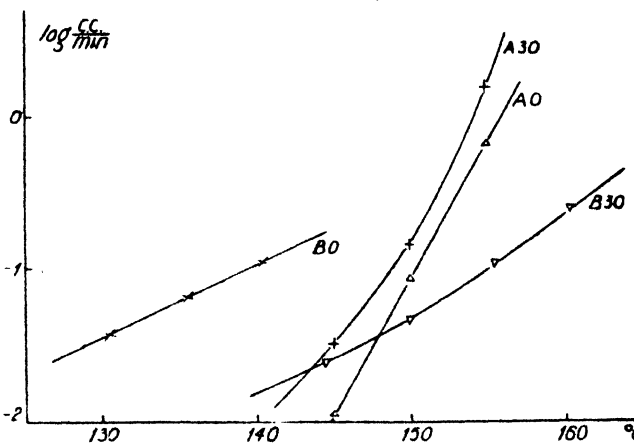


FIG. 7.—Oxidation rate against temperature for four oils.

Hence our choice of 155° C.

Conclusions.

The results indicate clearly that there is a marked difference in these oxidation curves concerning oils of different quality. Further comparative study with more samples and measurements, showing the correlation between this test and some other chemical changes in the oil, *e.g.*, acid rise, sludging, peroxide formation, etc., will, however, be required to determine whether the method is really suitable for a routine test. It seems as if the chief merit of the test consists in a quick elimination of quite unsuitable types, whereas a further differentiation of the remaining good ones has to be carried out by one of the more prolonged tests. At any rate, the manometer could be replaced by an automatic pressure recorder, in which case the operation of the device, now at constant volume, could be made extremely easy. It is intended to continue the investigation on the lines just mentioned.

Summary.

If oil is oxidised at about 150° C. under constant pressure in a relatively small closed space, and the decrease of the volume of the gas phase is plotted against time, curves are obtained which vary characteristically with the grade of the oil. The changes are the less pronounced, the curves the flatter, the poorer the oil, owing probably to production of volatile products, counteracting the effect of absorption of oxygen.

The method seems to be suitable for rapid testing of the stability of oils.

The author is much indebted to Professor R. V. Southwell, F.R.S., for facilities placed at his disposal; to Messrs. Metropolitan Vickers Electrical Co. Ltd., Manchester, for a grant enabling him to undertake this investigation; and to Messrs. Silvertown Lubricants for the samples of oil.

*Communicated from the Engineering Laboratory,
Oxford University.*

THE CHEMICAL KINETICS OF DIELECTRIC RELAXATION.

BY F. C. FRANK.

Received 13th August, 1936.

When one says, on the grounds of its dielectric behaviour, that a cetyl palmitate molecule in solid solution in paraffin wax rotates about as freely as if it were in a continuous fluid of the viscosity of castor oil, that is useful in enabling one to feel in imagination the restraint upon the molecule, but in the end one must admit that the model is too remote from the actual conditions to be more than a helpful analogy. We have tried in the past to defend the model by supposing the ester grouping sufficiently incompatible with the hydrocarbon crystal to break it up in its immediate neighbourhood into a disordered condition approaching that of an oil: but this defence will not stand. That there can be no laminar flow is but one of many difficulties in the way of it. For example, when we change to butyl stearate instead of cetyl palmitate we find the maximum of dielectric loss at 7 MC. shifted down some 44° C in temperature. Taking a temperature coefficient of "viscosity" from the cetyl palmitate results, we find this corresponds to a change by a factor of 50. Yet neither the molecular volume nor any molecular dimension has been reduced by such a factor. The temperature coefficient is also different, and different again for a solid solution of cetyl alcohol in the wax. Thus we learn that both the "viscosity" and its temperature coefficient depend on the solute as well as upon the solvent.

It is clear that when we are applying the conception of viscosity to the movements of a single molecule, we must examine the discontinuous molecular processes which produce viscosity. Several theoretical discussions of viscosity ^{1, 2, 3, 4} are suggestive, though none is quite directly applicable to our case. We must go to something more fundamental than these, to which they are related, the theory of unimolecular reactions.

When electric stress is applied to some materials containing polar molecules a statistical departure from random orientation is impressed upon them. If the stress is abruptly removed, the impressed orientation, which is observable as an electric displacement within the material, decays with a finite relaxation time. This decay has hitherto been treated as a rotational diffusion by Brownian movement: but it is equally analogous to a *cis-trans* isomerism. The proposal of the present paper, therefore, is to apply the equations of chemical unimolecular reaction to the process of dielectric relaxation.

In practice we do not adopt the difficult expedient of abruptly removing an electric stress, but apply a sinusoidally alternating voltage to the material. Then for periods of alternation near to the relaxation time τ for orientation of the polar molecules, we find an energy absorp-

¹ J. Frenkel, *Z. Physik*, 1926, **35**, 664; *Nature*, 1930, **125**, 581.

² J. S. Dunn, *Trans. Faraday Soc.*, 1926, **22**, 401.

³ E. N. da C. Andrade, *Phil. Mag.*, 1934, **17**, 497, 698.

⁴ H. Eyring, *J. Chem. Physics*, 1936, **4**, 283.

tion in the material and a dispersion of its dielectric constant: the dielectric constant passes through its mean value and the imaginary dielectric constant (which is a measure of the absorption) through its maximum when the period of alternation is approximately $2\pi\tau$. (See Fig. 1a.)

Debye introduced an inner friction constant governing molecular rotation in his treatment of the relaxation (ref. 5, p. 85). Tentatively he estimated this by the Stokes' formula for rotation of a sphere in a viscous fluid, obtaining

$$\tau = \frac{4\pi\eta a^3}{kT}$$

(where η is viscosity, a molecular radius, k Boltzmann's constant.), to connect τ with at least a reasonable order of magnitude for the molecular radius. The success with hydroxylic liquids was unexpectedly good, but since then more normal systems have all shown excessively small radii. The maximum loss for these liquids occurs, however, in a highly inaccessible range of frequency, and the best examples of the Debye loss curves have been found with solids or semi-solids to which this formula can only be applied by introducing an entirely fictitious viscosity.

We shall not be able to distinguish in practice (at least, with present resources) between the Brownian rotation and chemical reaction mechanisms. According to the former, the molecule loses the impressed orientation by a succession of random movements, the trace of its original position becoming less and less after each. According to the latter, the molecule is supposed to make larger and less frequent movements, one of which destroys practically all trace of the original orientation (at other times oscillating about a temporarily fixed mean position). There will be very little difference when we observe the integrated effect of many

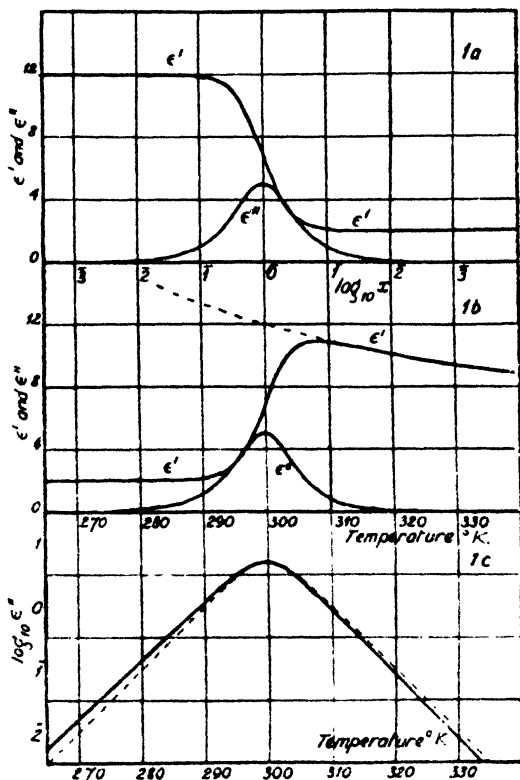


FIG. 1.—Theoretical variation of dielectric constant (ϵ') and loss (ϵ''). (a) with frequency and (b), (c), with temperature.

For (b), $\log_{10} \tau$ is assumed to change by 1 for 10° change of temperature, and ϵ_1 is given a temperature variation shown by the broken curve as an ideal case of orientation polarisation.

In (c) the ϵ'' curve of (b) is redrawn on a logarithmic scale. The symmetrical broken curve corresponds to a constant ϵ_1 or the ϵ'' curve of (a).

molecules. Moreover, there will be no sharp borderline distinguishing systems to which one or the other treatment should be applied, though we can often say which is the appropriate treatment in particular cases. When the polar solute molecule is much larger than the molecules of solvent the Brownian movement treatment is applicable. Where we have a molecule of variable orientation embedded in a crystalline solid (as for example our solid solution of cetyl palmitate in paraffin wax), the unimolecular transformation treatment is fairly evidently more suitable. This is also the natural corollary of the special treatment tentatively suggested by Debye for ice (ref. 5, p. 104).

In the simplest sort of case, we should suppose the polar molecule undergoing rotational oscillations with a certain frequency ν about a fixed mean position, until it received (as a thermal fluctuation) enough energy of oscillation ϵ to lift it over a potential barrier, when it would have the chance to settle down into other minima of potential energy with different orientations. In such a case the activation would be in two quadratic terms, and the rate of the de-orientation reaction would be

$$2\nu e^{-\epsilon/kT},$$

since the attempt to leave the potential valley can be made twice in each vibration, while the probability of success is given by the Boltzmann term. This is analogous to Frenkel's viscosity theory, and the simplest class of chemical reactions: but it makes the supposition that the environment of the molecule is permanent and unvarying, whereas in reality it will also be subject to thermal fluctuations. Hence we may anticipate in some cases at least the more complicated behaviour characteristic of activation in many degrees of freedom, producing in this case a general loosening of the material in the neighbourhood of the polar molecule. Since the limits of the system here include the whole crystal, whereas in the majority of unimolecular chemical reactions it is only a molecule of a hundred atoms at the most, we may anticipate extreme values of the number of degrees of freedom activated, providing an interesting extension to the class of unimolecular reactions. The effects of activation in many degrees of freedom are to produce large values both of C and A in the Arrhenius equation

$$k = Ce^{-A/RT}.$$

Debye represented the decay of orientation as a simple exponential process

$$\phi(t) = e^{-t/\tau}$$

t being time, τ the relaxation time (ref. 5, p. 84), so that when we represent it as a unimolecular reaction the velocity constant must be taken as $1/\tau$. Using this expression Debye deduced the following equations defining the behaviour in an alternating field:

$$\epsilon' = \epsilon_0 + \frac{\epsilon_1 - \epsilon_0}{1 + x^2}$$

$$\epsilon'' = \frac{\epsilon_1 - \epsilon_0}{1 + x^2} x$$

where

$$x = \frac{\epsilon_1 + 2}{\epsilon_0 + 2} \omega \tau,$$

ω is the circular frequency, ϵ_1 the dielectric constant at low frequency, ϵ_0 that at high frequency, ϵ' and ϵ'' the real and imaginary parts of the complex dielectric constant ϵ^*

$$\epsilon^* = \epsilon' - i\epsilon''$$

(Fig. 1a).

There is experimental evidence that $\log \tau$ varies nearly linearly with temperature. This is equally in harmony with the temperature variation of viscosities and of velocity constants. When the temperature coefficient of τ is large, as in the experimental cases considered in this paper, we may neglect other sources of variation with temperature (chiefly the change of $\epsilon_1 - \epsilon_0$), and attribute all the temperature variation at constant frequency of ϵ' in the range of maximum dispersion, and ϵ'' throughout its measurable range, to the change of τ : as a result, the change of these quantities with temperature is closely similar to their change with the logarithm of the wave-length. (Fig. 1b.)

To Derive τ and its Temperature Coefficient from Loss Measurements.

In an ideally simple case in which $\log \tau$ is a strictly linear function of the temperature T , and ϵ_1 , ϵ_0 and ω constant, the graph of $\log \epsilon''$ against T becomes a hyperbolic curve approximating closely, except near the apex, to a pair of straight lines of equal and opposite slope (Fig. 1c). The slope of these asymptotes is $\frac{d}{dT} \log \tau$. The same is true of the asymptotes of the logs of power factor, dipole conductivity, and in fact all the quantities in terms of which dielectric loss is specified. This is one of the most valuable relations for deriving the required information from experimental results, since it can be applied if necessary to results measured at only a single frequency. The method of logarithmic plotting against temperature is also a much more sensitive test of departure from ideal behaviour than the usual direct plot. Its only disadvantage is that it throws reliance upon measurements of the dielectric loss away from the maximum, where it may be very small. There will be some tendency to underestimate the temperature coefficient when there are not enough accurate points sufficiently far from the maximum.

Where it is necessary to deal with measurements near to the maximum, the ideal loss curve can be described to a sufficient approximation by

$$\frac{\epsilon''}{\epsilon''_{\max.}} = y = \frac{2e^{\alpha/T_m}}{1 + e^{2\alpha/T_m}}$$

when

$$\tau = k_1 e^{\alpha/T} \approx k_1 e^{-\alpha/T_m}$$

so that

$$\frac{d}{dT} \ln \tau = -\frac{\alpha}{T^2},$$

t is $(T - T_m)$, where T_m is a temperature in the middle of a small range—here the temperature at which ϵ'' is maximum.

The same formula applies to dipole conductivity, and in the special case of a dilute solution of polar solute in non-polar solvent (which in any case is the only one in which ideal behaviour can be expected), also to the power factor and related quantities.

From this expression we obtain

$$e^{\alpha t/T_m^2} = \frac{1}{y} \pm \sqrt{\frac{1}{y^2} - 1}$$

and

$$dy/dt = \frac{2\alpha}{T_m^2} \cdot \frac{e^{\alpha t/T_m^2} - e^{3\alpha t/T_m^2}}{(1 + e^{2\alpha t/T_m^2})^2},$$

whence it is possible to derive expressions for the width of the curve ($t_2 - t_1$), or its slope for any particular value of y . The use of these quantities should, however, be avoided when possible, since any sort of inhomogeneity in the material, which is to be anticipated in all cases for which extensive measurements near the loss maximum have yet been made, causing τ to have not a single value but a small range, will lead to serious underestimates of the temperature coefficient of τ by this method. Another objection to it is that in measuring with solids at high frequency experimenters sometimes allow the wave-length to change with the changing dielectric constant of the material in its dispersion range, a considerable practical simplification which complicates the theoretical form of the curve near its apex. When this is not the case, comparison of this value with that obtained in another manner can be used to measure the degree of inhomogeneity.

Where we have measurements at several frequencies we can obtain what is practically $\frac{d}{dT} \log \tau$ by plotting \log (frequency) against temperature of maximum loss and measuring the slope of the graph, which should be practically a straight line. When available, this is generally to be preferred to other methods, but entails a large amount of experimental work.

To Derive τ .

When a maximum of dielectric loss is observed, the procedure is easy enough.

(1) The imaginary dielectric constant ϵ'' , the dipole conductivity (proportional to $\omega\epsilon''$ and to the power loss with constant voltage) and the dipole resistivity (proportional to ϵ''/ω and to the power loss with constant current) all reach their maximum against temperature when $x = 1$, i.e., when

$$1 - \frac{\epsilon_1}{\epsilon_0} + 2 = \frac{\epsilon_1}{\epsilon_0} + 2 = 2\pi\nu.$$

(2) $\epsilon''/\epsilon' = \tan \delta$, commonly called the power factor, the phase angle δ , and the true power factor $\sin \delta$, all reach their maximum when

$$x = \sqrt{\frac{\epsilon_1}{\epsilon_0}},$$

i.e., when
$$\frac{1}{\tau} = \frac{\epsilon_1 + 2}{\epsilon_0 + 2} \cdot \sqrt{\frac{\epsilon_0}{\epsilon_1}} \cdot \omega.$$

(3) We need not consider here the absorption coefficient specified in the optical manner which is occasionally used in work at very high frequencies and has yet another condition of maximum.

When the measurements do not include a maximum, it is possible to extrapolate from the asymptote provided the magnitude of the loss at maximum is known. This can be calculated from $(\epsilon_1 - \epsilon_0)$

$$\epsilon''_{\text{max.}} = \frac{1}{2}(\epsilon_1 - \epsilon_0)$$

or from the dipole moment and concentration of a solute in dilute solution. We have on the low frequency, high temperature, side:

$$\tau = \frac{1}{2\omega} \cdot \frac{\epsilon_0 + 2}{\epsilon_1 + 2} \cdot \frac{\epsilon''}{\epsilon''_{\text{max.}}};$$

on the high frequency, low temperature, side:

$$\tau = \frac{2}{\omega} \cdot \frac{\epsilon_0 + 2}{\epsilon_1 + 2} \cdot \frac{\epsilon''_{\text{max.}}}{\epsilon''}.$$

When (ϵ''/ϵ') is used instead of ϵ'' in these expressions, they must be multiplied by $\sqrt{\frac{1}{\epsilon_0}}$.

To Derive τ and its Temperature Coefficient from Dielectric Constant Measurements.

ϵ' reaches its mean value $\frac{1}{2}(\epsilon_0 + \epsilon_1)$ under the conditions in which ϵ'' is maximum. At this point of inflection the slope is

$$\frac{d\epsilon'}{dT} = -\frac{\epsilon_1 - \epsilon_0}{2} \frac{d}{dt} \ln \tau,$$

to the same degree of approximation as before. The correction to be added to this when the orientation polarisation varies with temperature according to the Debye theory is

$$-\frac{\epsilon_1 - \epsilon_0}{2T} \frac{(\epsilon_1 + 2)}{(\epsilon_0 + 2)}$$

which is negligible when $\frac{d}{dt} \ln \tau$ is as large as it is in cases discussed in this paper.

Analysis of the Reaction Velocity Equation.

Having obtained by one of the above methods a value of τ and of $\frac{d}{dT} \ln \tau$ at a temperature T , we can evaluate the constants of the Arrhenius equation for reaction velocity

$$\frac{1}{\tau} = k = Ce^{-A/RT}.$$

Thus the α used in the previous section is identical with A/R . It is convenient to evaluate A/RT ($= -T \frac{d}{dt} \ln \tau$) as well as A and C . The value found for C now requires special consideration.

In the simplest case a value between 10^{13} and 10^{14} is expected. A larger value implies activation in many degrees of freedom. Hinshelwood⁶ gives an equation which may be brought into the form

$$k = C_1 \frac{e^{-(A/RT+f)} (A/RT+f)^f}{f!}.$$

⁶ C. N. Hinshelwood, *Kinetics of Chemical Change in Gaseous Systems*, 1933, p. 128.

Here C_1 is a constant having the normal value $10^{13} - 10^{14}$ and f has been written for Hinshelwood's $\left(\frac{n}{2} - 1\right)$. n is the number of quadratic terms in which activation energy is shared, so that f may be loosely regarded as one less than the total number of vibrations involved in activation. When f is large we can introduce the asymptotic formula for factorials:

$$f! \approx \left(\frac{f}{e}\right)^f \sqrt{2\pi f},$$

so obtaining

$$k = C_1 e^{-A/RT} \cdot \frac{1}{\sqrt{2\pi f}} \left(\frac{A/RT + f}{f}\right)^f.$$

C_1 may be conveniently taken as $\sqrt{2\pi} \times 10^{13}$ and f can then be ascertained by trial.

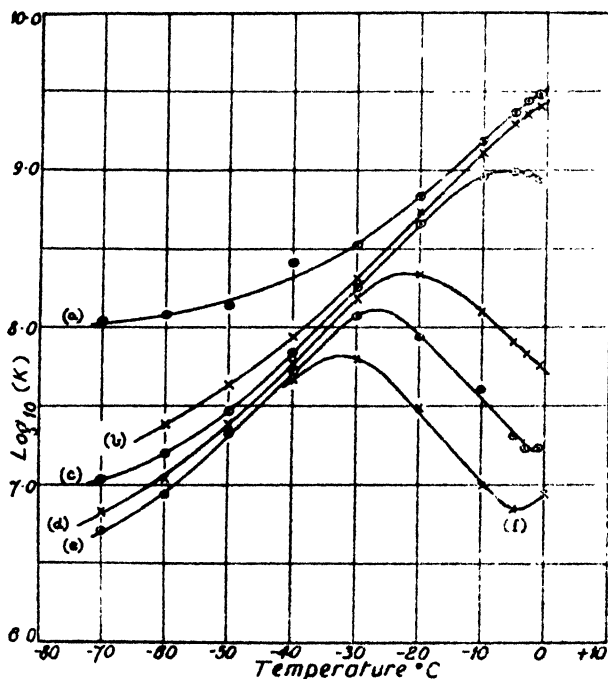


FIG. 2.—Dielectric loss (conductivity) of ice from measurements by Smyth and Hitchcock.

- (a) 60 kcs. (b) 20 kcs. (c) 5 kcs.
(d) 1 kc. (e) 0.5 kc. (f) 0.3 kc.

ling" effects) becomes: ⁴

$$k' = K \cdot \frac{F_a^*}{F_n} \cdot \frac{kT}{h} \cdot e^{-E_0/kT}.$$

K , the transmission coefficient, is generally taken as 1; F_a^* is the partition function of the activated state omitting the degree of freedom normal to the potential barrier and calculated using a zero E_0 higher than that used for F_n , the partition function of the normal state. All degrees of freedom which are the same in both states cancel so that in the simplest

It is to be noticed that if f varies continuously with temperature, the results will be in error. While f is increasing, A and f will be overestimated; while f is decreasing they will be underestimated; a stationary value will be estimated correctly.

The transition state treatment of reaction velocities nowadays preferred by some workers leads us to practically the same qualitative picture of the process of reaction. The general reaction equation (omitting "tunnel-

of all cases in which one vibration is converted to a translation by the activation process,

$$\frac{F_a^*}{F_n} = (1 - e^{-h\nu/kT})$$

which approximates to 1 when the frequency of the vibration is high. Our frequency factor C thus becomes $kT/h \approx 10^{13}$. However, quoting from Eyring, as a general phenomenon in reaction rates "with an abnormally high E_0 , there is in general associated an abnormally high F_a^*/F_n . The reason is that the large E_0 arises from loosening an abnormally large number of bonds (or from loosening very strong bonds), and this automatically means a large value for the ratio F_a^*/F_n ." The qualitative picture is therefore exactly the same.

Discussion of Some Experimental Cases.

(1) *Ice*.—The graph (Fig. 2) shows Smyth and Hitchcock's results for ice,⁷ logarithmically plotted. This should be compared with the direct graph of ϵ'' (*loc. cit.*,⁷ p. 4642). There are two points of departure from ideal behaviour: the linear portions of the curves on the low-temperature side are not coincident as they should be, and the curves rise above their linear extrapolations at the lowest temperatures. This is especially the case at the highest frequencies. These facts would be explained if there were a small secondary component of loss reaching its maximum at a slightly higher frequency or lower temperature than the range studied. It is true, since these deviations depend on measurements of the lower losses, that they may be due to experimental error; but no single source of error can produce them and the losses should still be quite large enough to measure accurately.

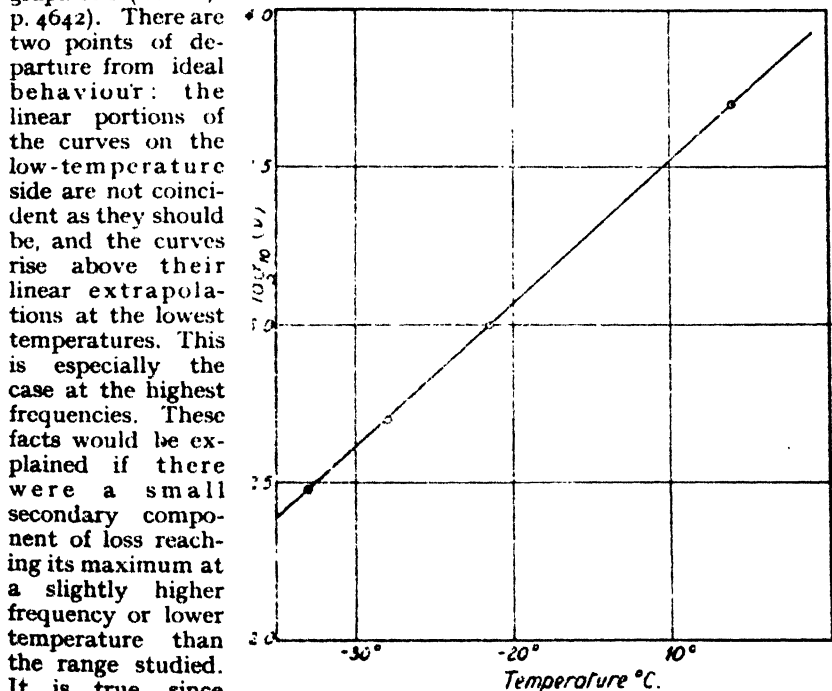


FIG. 3.—Frequency of maximum loss (conductivity) in ice.

The slopes of eight linear portions of the curves can be measured. They are found to be:

⁷ C. P. Smyth and C. S. Hitchcock, *J. Amer. Chem. Soc.*, 1932, **54**, 4631.

Ascending branches	60,	20,	5,	1,	0.5 k.c.
$-\frac{d}{dt} \log_{10} \tau =$	·038,	·040,	·041,	·041,	·041
Descending branches	1,	0.5,	0.3 k.c.		
$-\frac{d}{dt} \log_{10} \tau =$	·040,	·041,	·044		
Mean of all,	·041				
Mean temperature,	250° K.				
Frequency of max. ϵ'' at this temperature = 8.51×10^3 .					

By plotting $\log \nu_{\max.}''$ against temperature (Fig. 3), we get another value of $\frac{d}{dt} \log_{10} \tau = \cdot 045$, corresponding to $T_{\text{mean}} = 253^\circ \text{K.}$, for which $\nu_{\max.}'' = 1.17 \times 10^4$. From these two different results with $\epsilon_1 = 78$ and $\epsilon_0 = 3.0$:

T_{mean}	$-d/dt \ln \tau$	A/RT	A	$1/\tau$	C	f
250	·0945	23.6	11,700 cal.	8.55×10^4	1.45×10^{18}	2
253	·104	26.2	13,200 cal.	1.18×10^5	2.90×10^{18}	4 or 5

Of these, the latter is doubtless more accurate.

H. Eyring ⁴ has already suggested applying reaction velocity theory to this case. Roughly estimating $1/\tau$ at 0°C. as 60,000 (10^5 is nearer), and assuming that C would be normal ($= kT/h$), he estimated the activation energy as about 10,000 cal., which is not grossly wrong though it would not satisfactorily describe the temperature variation. The same method applied to some of the examples below would have given entirely false results.

In the same place Eyring makes a valuable suggestion that the relaxation times of the order 10^{-12} secs. found in normal solvents should be treated in the same way, as reactions with very low activation energies.

(2) **Solid Solutions in Paraffin Wax.**—The experimental information for the butyl stearate solution is very limited, so that the conclusions from it must not be regarded as finally accurate, but they are of the highest importance in comparison with the other paraffin-wax systems (Fig. 4). There is a clear break in the curve between 17 and 23° . In spite of the fact that the measurements refer to rather small losses, it seems quite out of the question that so large a deviation can be attributed to experimental error. Below this temperature the relaxation is a reaction with a normal frequency factor and an activation energy of 6800 calories. Above this temperature we have a reaction with nearly three times the activation energy and consequently a much larger frequency factor, indicating activation in about 60 degrees of freedom. It is a well-known possibility in chemical kinetics, when a reaction can proceed by alternative mechanisms, for the reaction of higher activation energy to supersede the other above a certain temperature at which they have the same velocity. Of course, the frequency factor must be larger, or the reaction of higher activation energy would always be much slower than the other.

[Note added in proof, 17th October, 1936: Further work by Mr. Sillars confirms the change of slope shown in Fig. 4 but gives other indications which may demand revision of the interpretation given here. It is however allowed to stand as a convenient introduction to the case of cetyl palmitate.]

The cetyl alcohol case requires no special discussion. The anomalies for power factors less than 2×10^{-4} may fairly be ascribed to experimental error (Fig. 4).

The cetyl palmitate curves require a little care in interpretation (Fig. 5). In the first place, the very steep lines above 41° are considered to be due to a polymorphic transition of the wax, which does not take

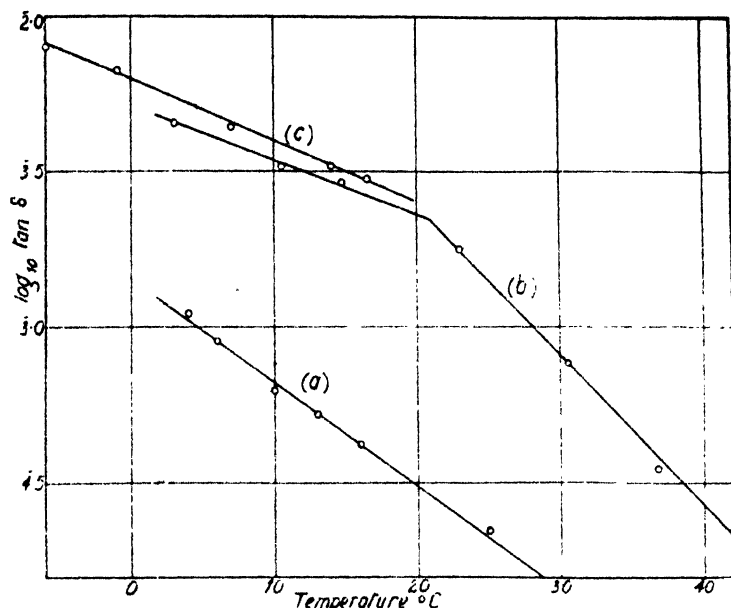


FIG. 4.—Dielectric loss in paraffin wax solid solutions, (a) 4.57 per cent. Cetyl alcohol—measurements by W. Jackson,⁸ (b), (c) 5.6 per cent. Butyl Stearate, two series of measurements by R. W. Sillars (unpublished).

place at a single temperature because the wax is not a single substance. The high apparent activation energy of about 60,000 cal. has, therefore, no significance. Jackson, in fact, observed this transition, and was rather

SOLID SOLUTIONS IN PARAFFIN WAX.

	Mean T .	$-\frac{d}{dT} \ln \tau$.	$\frac{A}{RT} = -T \frac{d}{dT} \ln \tau$.	$A = -RT^2 \frac{d}{dT} \ln \tau$.	$1/\tau = 2\pi\nu$ at Mean T .	C .	f .
Butyl Stearate .	281	0.437	12.6	Calories.			
	304	0.110	33.4	6,800	3.00×10^8	8.65×10^{12}	0
				20,200	1.51×10^9	4.67×10^{22}	—
Cetyl Alcohol .	287	0.773	22.2	12,600	2.43×10^9	1.0×10^{13}	22
Cetyl Palmitate : by log plotting, mean of 3	285	0.892	25.4	14,400	3.75×10^6	3.8×10^{17}	8
" " 3	304	0.188	57.1	34,500	8.04×10^7	5.0×10^{22}	140
" " 2	318	0.301	(95.7)	(60,400)	—	—	—
by shift of maxima	296	0.171	50.5	29,600	2.38×10^7	1.9×10^{20}	90

(Figures for all but butyl stearate are derived from the work of W. Jackson.⁸ Those for butyl stearate are from unpublished work by R. W. Sillars with the same apparatus.)

⁸ W. Jackson, *Proc. Roy. Soc., A*, 1935, 150, 197.

surprised because he supposed it was without effect upon his dielectric loss curves.⁹ This demonstrates the superior informativeness of the logarithmic graph. Below this temperature the curves are still clearly unsym-

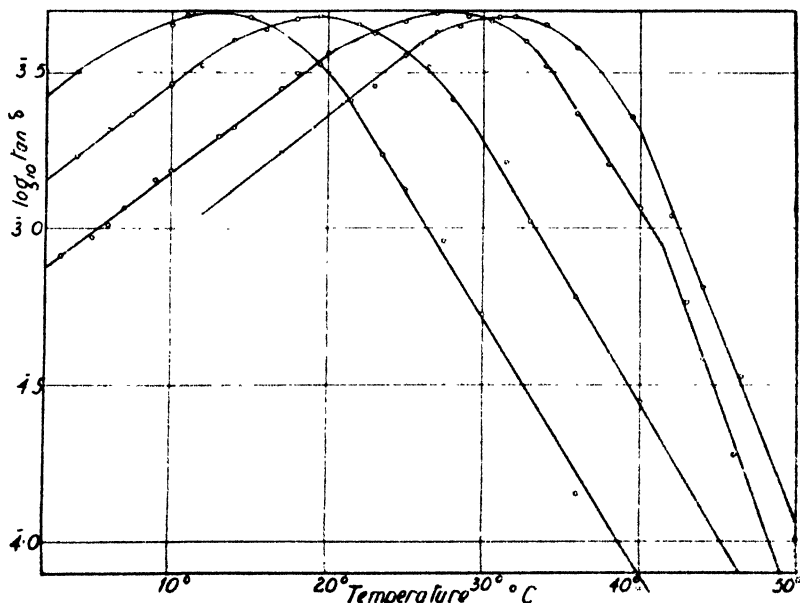


FIG. 5.—Dielectric loss in 4.78 per cent. solid solution of cetyl palmitate in paraffin wax. Measurements by W. Jackson.⁹

metrical, most probably owing to a change in the temperature coefficient of τ in the neighbourhood of 23° , similar to the change at about the same temperature in the butyl stearate case. In this case it is still an abnormally

fast reaction below this temperature, but a very fast one above it.

There is an upper limit to the permissible value of f , determined by the number of atoms involved in the activation, which cannot be less than about $f/3$. In a gas reaction this limit is imposed by the number of atoms in the individual molecule, and the highest value yet found is about 25 in the decomposition of azoisopropane.¹⁰ The value of 140 found for the cetyl palmitate solution above 23° C. cannot well be ascribed to activation by energy concentrated in one molecule, while this becomes impossible in the case of "permitol" described below. However, it

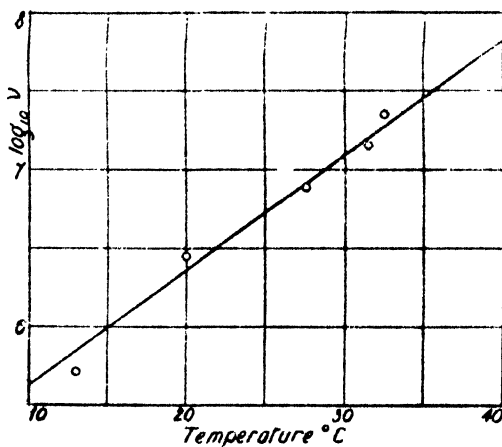


FIG. 5a.—Frequency of maximum loss in cetyl palmitate—paraffin wax solid solution.

⁹ W. Jackson, *Trans. Faraday Soc.*, 1935, **31**, 169.

¹⁰ H. C. Ramsperger, see G. B. Kistiakowsky, *Chem. Rev.*, 1935, **17**, 49.

becomes quite possible if we bring in four or more nearest neighbours as well as the central molecule under consideration; while there is no *a priori* objection to spreading the activation much further, so that the only limit is imposed by the number of atoms in the crystal.

It appears that it might be profitable to correlate this experimental evidence of the existence of activation in a very large number of degrees of freedom in these paraffin-wax systems with the theory of co-operative effects in molecular rotation in such crystals.^{11, 12, 13} Muller's X-ray crystallographic studies¹⁴ of the higher normal paraffins show that above about 20° C. the crystal shows a gradual change of form, with all the marks of a co-operative phenomenon. The change in, say, $C_{25}H_{52}$ may be readily interpreted as due to rotational oscillation of the hydrocarbon chains about their axes: this makes the chain behave as if it had more nearly cylindrical symmetry and the crystal structure approach more nearly the hexagonal form: this in turn permits freer rotation and the change builds up rapidly, the *b*-axis ceasing to expand and starting to contract. $C_{25}H_{52}$ becomes

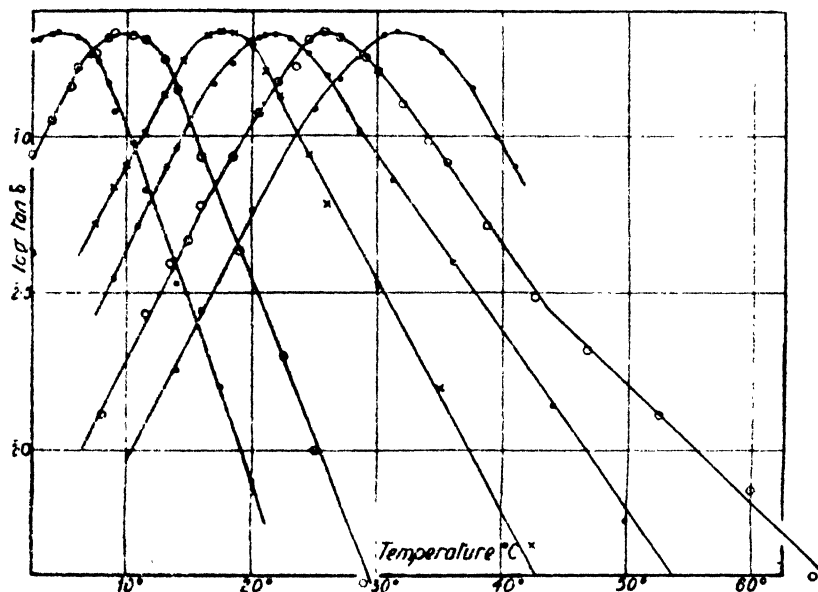


FIG. 6.—Dielectric loss in chlorinated diphenyl ("Permitol"). Measurements by W. Jackson.¹⁵

hexagonal at 45° C., and melts at 46° C. In the higher members, the co-operative effect is so strong as to produce an abrupt transition at a certain stage. It is remarkable that these co-operative effects appear at about 20°, which is also the temperature in the neighbourhood of which the rotation of ester molecules in the waxes changes its mechanism to a process governed by activation in many degrees of freedom.

(3) "Permitol."—This synthetic dielectric material, chemically a mixture of isomers of tetrachlorodiphenyl, is of special interest because it is in the physical condition of a glass just above its softening range. It pours slowly at room temperature, and can be cracked and chipped if

¹¹ L. Pauling, *Physic. Rev.*, 1930, **36**, 430.

¹² R. H. Fowler, *Proc. Roy. Soc., A*, 1935, **149**, 1.

¹³ W. L. Bragg and E. J. Williams, *ibid.*, 1934, **145**, 699 (for the simpler theory of co-operative phenomena in another connection).

¹⁴ A. Muller, *ibid.*, 1932, **138**, 514.

¹⁵ W. Jackson, *ibid.*, 1935, **153**, 158.

cooled in ice and salt. Actual viscosity measurements are given in the original paper.¹⁵ Since we have here dielectric-loss measurements covering a very wide range (Fig. 6), the opportunity has been taken to test all the various methods outlined above for deriving $\frac{d}{dT} \ln \tau$ from experimental data, with the following results (Fig. 7) :

(a) The change with frequency of the temperature of maximum loss gives, as expected, higher values than any other method. These values are taken as the best.

(b) The asymptotes of the descending branches of the logarithmic graph give also quite good and consistent results. Their uniform lowness compared with the results of (a) should be regarded rather as an underestimate by 5° of the mean temperature to which the slopes correspond ; a natural error arising from the regular decrease of slope with rising temperature which makes the curves appear to reach their asymptotes too soon.

(c) The slopes of descending branches at half-height measured on the original graphs are in agreement with (b), but show wider scatter.

(d) All results referring to ascending branches of the curves are low. This might be due to inhomogeneity, in particular to the presence of a small percentage of dipoles of rather higher mobility than the rest, which cannot be unexpected in such a mixture as this.

(e) Values calculated from widths at half-height are intermediate between those of (b) and (c) on the one hand, and (d) on the other, as is to be expected.

The results of (a) only are used in forming the velocity equations. *A* is seen to be rather large throughout the range, rising as temperature falls but appearing to become stationary below 10° C. *C* is also anomalously high throughout the range, varying in sympathy with *A*, and correspondingly *f* approximately doubles in value as

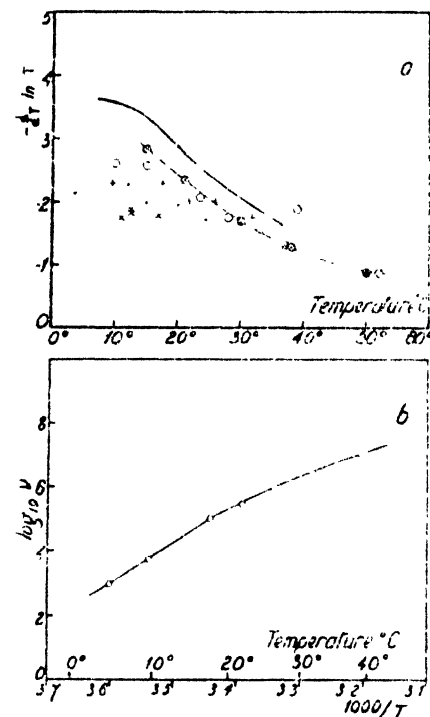


FIG. 7a.—Temperature variation of the temperature coefficient of τ in chlorinated diphenyl, variously determined.

(a) —————; (b) —⊗—; (c) ⊙; (d) × asymptotes, * slopes; (e) +; (f) ●, a directly measured temperature coefficient of viscosity.

FIG. 7b.—Temperature variation of frequency of maximum loss in chlorinated diphenyl.

the material is cooled. However, since *f* is varying, these quantities (*A*, *C* and *f*) will all be underestimated above 15° C.; but if, as it appears, *f* is stationary below this temperature, the results in the first three rows should be approximately correct. The rest must only be taken in qualitative significance. Subject to this limitation, they are what may reasonably be expected in a substance on the point of setting to a glass. As temperature falls, the number of bonds which must be loosened, and the increment of energy required to do so, to make a molecule free to turn about, steadily increases.

PERMITOL.

100/T.	T.	A.	A/RT.	-d/dT ln τ .	ν .	1/ τ .	C.	f.
		Kcals.						
3.55	281.7	56.5	101.1	.358	4.315×10^3	3.69×10^3	2.3×10^{47}	200
3.5	285.7	56.7	100.0	.349	1.80×10^4	1.54×10^4	4.2×10^{47}	220
3.45	289.9	53.2	92.5	.319	7.50×10^4	6.41×10^4	8.1×10^{44}	200
3.4	294.1	40.8	80.2	.272	2.60×10^5	2.22×10^5	1.4×10^{40}	160
3.35	298.5	42.0	70.9	.237	7.94×10^5	6.79×10^5	3.8×10^{36}	130
3.3	303.0	37.5	62.3	.205	2.16×10^6	1.85×10^6	2.6×10^{32}	110
3.25	307.7	34.6	56.6	.184	5.25×10^6	4.49×10^6	1.7×10^{31}	90

$$\frac{1}{\tau} = 2\pi\nu \left(\frac{\epsilon_1 - 2}{\epsilon_0 + 2} \right) \sqrt{\frac{\epsilon_0}{\epsilon_1}} \quad 2\pi \times 1.36\nu \text{ when } \epsilon_1 = 4.8, \epsilon_0 = 2.8.$$

The close parallelism between τ and viscosity in this material is a confirmation of the close connection between the ultimate mechanisms of both, which is obviously seen to be required when any of the theoretical treatments of viscosity mentioned above is examined in comparison with the present treatment of dielectric relaxation. It is to be noticed that the temperature coefficient of τ and η in "Permitol" and of τ in the paraffin-wax solid solutions is enormously greater than the temperature coefficient of viscosity in most liquids: the temperature coefficient of η for molten paraffin wax is about 0.007 corresponding to an activation energy of 1.6 k. cals.

Kassel¹⁶ has shown that anomalously high apparent activation energies can result when the reaction proceeds through several reversible stages in cascade before the final effective step. This must, therefore, be admitted as alternative to the assumption of activation in many degrees of freedom: but the latter is nevertheless preferred at present as more readily accounted for in the physical nature of the system.

Summary.

The theory of unimolecular chemical reaction velocities is applied to the process of change of orientation of a polar molecule in a material showing dielectric loss and dispersion. The requisite analysis of experimental data is explained. Experimental results for three different types of physical system are considered:

- (1) Ice,
 - (2) Solid solutions of polar substances in paraffin wax,
 - (3) A polar organic glass at the top of its softening range ("permitol").
- (1), and apparently cases in (2) at low temperature, present fairly normal unimolecular reactions; the rest present very fast reactions, as though activation involved many degrees of freedom. This is thought to be consistent with their physical nature.

Acknowledgment is due to the Department of Scientific and Industrial Research for a grant, to the author's laboratory collaborators for experimental figures placed at his disposal, and to Mr. C. N. Hinshelwood for a discussion.

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Oxford.*

¹⁶ L. S. Kassel, *J. Amer. Chem. Soc.*, 1929, **51**, 1136.

ON THE MOVING BOUNDARY METHOD OF MEASURING CATAPHORESIS.

BY J. J. BIKERMAN.

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The observed velocity of the moving boundary between a sol and a supernatant liquid depends on the nature of this liquid. Attempts to eliminate its influence or find out which supernatant liquid gives the correct value, *i.e.*, the mobility of the sol particles within the sol, have not given a satisfactory result.¹

If, however, we use as supernatant liquid for a given sol another sol which is practically identical with it but of a different colour (or refractive index), the rate of movement will obviously correspond closely with the particle mobility within the homogeneous sol.* We know, for instance, that gold sol particles covered with gelatin move with the same velocity as gelatin particles alone;² observation of the boundary between a pure gelatin solution and a solution of gelatin infected with gold would, therefore, give the correct mobility.†

One would not expect, however, that the boundary between two gelatin solutions would move at a rate appreciably different from that of the boundary between a gelatin-in-buffer-solution and the unmixed buffer solution, because small amounts of gelatin change the electrical conductivity and other relevant properties of the relatively concentrated buffer solution hardly appreciably. The largest differences between the mobilities measured in the old and in the new way should occur when very many highly charged particles are suspended in a solution containing but few ions. An arsenic trisulphide sol would be a perfect example of such a sol if the common formation equation $\text{As}_2\text{O}_3 + 3\text{H}_2\text{S} = \text{As}_2\text{S}_3 + 3\text{H}_2\text{O}$ were complete, but, even after taking in account the forming of oxidation products of H_2S and so on, As_2S_3 seemed to be suitable. As indicator HgS was used.

I observed, accordingly, the moving boundary between a mixed As_2S_3 — HgS sol and an As_2S_3 sol. The constant sharpness of the boundary and the concordant mobilities of direct and reverse movements showed the practicability of the method. To prove that the visible mobility was identical with the mobility of As_2S_3 particles the transport of the sol was measured in the same apparatus both by the Hittorf and by the

¹ J. N. Mukherjee, *Proc. Roy. Soc., A*, 1923, **103**, 102; J. Bikerman, *Z. physik. Chem.*, 1925, **115**, 261; *Koll. Z.*, 1927, **42**, 293; W. Hacker, *Koll. Z.*, 1933, **62**, 37; *Kolloid-Beihfte*, 1935, **41**, 147; D. C. Henry and J. Brittain, *Trans. Faraday Soc.*, 1933, **29**, 798; S. Komagata, *Res. Electrotechn. Labor. Tokyo*, 1933, No. 348.

* This device is reminiscent of the measurement of self-diffusion with radioactive indicators.

² W. Reinders and W. M. Bendien, *Rec. trav. chim. Pays-Bas*, 1928, **47**, 977; E. B. R. Prideaux and F. O. Howitt, *Proc. Roy. Soc., A*, 1929, **126**, 126.

† Such experiments (with gelatin-kieselguhr against gelatin) were published by A. L. Roberts and J. C. Carruthers, *J. Physic Chem.*, 1936, **40**, 703, just before my work was accomplished.

moving boundary method; the results were consistent. We may, therefore, conclude that the boundary moves at the same rate as As_2S_3 particles in an almost homogeneous sol.

The new method is obviously inapplicable when the mobility of an old sol is to be determined. This mobility, however, will generally be a purely fortuitous magnitude. If reliable figures for the mobility of a sol are required in order to compare them with other properties of the sol, the "supernatant liquid" may be prepared together with the sol and the new method may be applied.

Apparatus.

The apparatus chiefly used in present experiments was a modification of the "sheared boundary" apparatus of MacInnes.³ As in MacInnes' pattern, the resistance glass tubes A and B were fitted into the discs *a* and *b*. The disc *a* could be turned so as to make A a prolongation of B and to form a boundary in their separation surface. The section of the tubes was 0.202 cm.². A new kind of electrode vessel had to be adopted since colloid solutions are more sensitive to traces of electrolytes (electrolysis products or salts of an unpolarisable electrode) than ionic solutions. When, for instance, a Zn/ZnCl_2 electrode was used, much As_2S_3 coagulated in contact with ZnCl_2 solution and the resulting streaming of the liquid carried some zinc ions outside the electrode cell.*

Satisfactory results were obtained with electrode vessels shown in Fig. 1. C is a copper wire in a copper chloride solution, G is a 3.5 per cent. gelatin gel containing 0.001 N NH_4Cl , the tubes T (0.38 cm. diameter) and U prevented the mixing of the electrolysis products with the sols in A and B. The filling of A and B was facilitated by using rubber stoppers and the taps *t*. As no special suspension of the apparatus⁴ was employed the boundary was only sharp when the density difference between both layers was considerable.

The "sheared boundary" arrangement presents two inconveniences: the impossibility of observing the boundary from the first moment of its formation and the difficulty of keeping clean the lubricated ends of the tubes and the holes in the discs. The method possesses, however, two important advantages: (a) the boundary is formed with but small

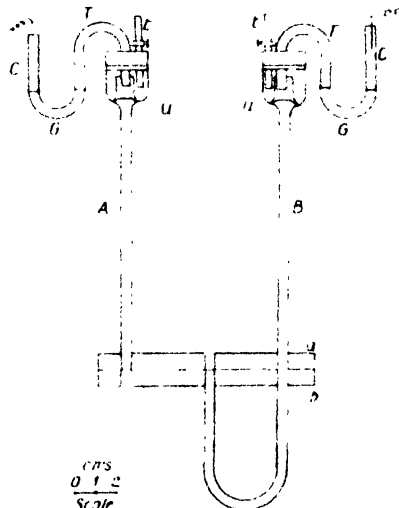


FIG. 1.—(U is intended to refer to the small tube inside the electrode cell.)

³ D. A. MacInnes and L. G. Longworth, *Chem. Reviews*, 1932, 11, 171.

* With such electrodes I sometimes observed the uprising of the lower liquid in "chimney shaped" regions as described by MacInnes, Cowperthwaite and Huang, *J. Amer. Chem. Soc.*, 1927, 49, 1710. MacInnes explained the phenomenon as due to a preferential warming by the current of the lower solution, which in his experiments was of lower conductivity. The explanation is not applicable to my observations, as the "chimneys" appeared only when the boundary rose and did not appear at reversal of the current although the asymmetrical heating does not depend on the current direction.

⁴ D. A. MacInnes, I. A. Cowperthwaite and T. C. Huang, *J. Amer. Chem. Soc.*, 1927, 49, 1710.

disturbance, (b) if it is not sharp enough we can let out a drop each from tubes A and B and establish a new boundary without rejecting the whole solutions.

In the transference experiments the tubes T were composed of two pieces ground together; the outer piece contained copper solution and gelatin gel, the inner piece was filled with the "supernatant" sol. After the experiment both pieces were separated and the contents of the inner piece added to the sol in A. The sol, then, was precipitated with HCl and As_2S_3 weighed. The most important error in the analysis originates in the difficulty of removing the As_2S_3 precipitate from the gelatin surface without picking up some gelatin.

Solutions.

The connection between the HgS and the As_2S_3 in the lower sol had to be made as intimate as possible; the conductivity of the mixed sol had to be nearly equal to the conductivity of the upper sol.

A saturated solution of yellow HgO in boiling water* was cooled and precipitated with hydrogen sulphide. To this sol a solution of As_2O_3 was added and H_2S conducted through the mixture; it was expected that HgS particles would function as nuclei for As_2S_3 . A part of the HgS formed, however, distinct grains which sedimented within some days or weeks. The remainder was stable but partly consisting of larger particles than the As_2S_3 sol.

By adding an arsenic trioxide solution to water which had been boiled for the same time as the HgO solution in an identical flask and saturated with H_2S , and treating the sol thus formed in exactly the same manner as the HgS- As_2S_3 mixture, we get sols whose conductivity sometimes coincides with the conductivity of the mixture, but may differ, too, by some 30 per cent. If a "subnatant liquid" for a given As_2S_3 sol is required, there is no difficulty, however, in obtaining it by mixing together two preparations of the mixture HgS- As_2S_3 made at the same time as the preparation of the As_2S_3 sol, or by mixing a HgS- As_2S_3 sol with the As_2S_3 sol. Since the conductivity of As_2S_3 solutions is not constant the subnatant liquid is adjusted shortly before the experiment.

In the experiments 4, 5, and 6 of Table I. the conductivities were equalized by adding slightly different amounts of NH_4Cl in an extreme case 0.00105 mol./l. NH_4Cl to the lower sol and 0.00100 mol./l. to the upper sol. It is generally known that such differences do not affect the mobility appreciably.

The arsenic trisulphide sols contained more than 8 gms. As_2S_3 per liter, while the concentration of HgS was less than 0.2 gms. per liter. The difference between the densities of the two layers would, therefore, be too small if the As_2S_3 concentration were exactly the same. The lower solutions were, accordingly, prepared with a surplus of about 5 per cent. As_2S_3 , or with the addition of some sugar. The mobility of colloid particles is not affected by such small differences in the sol concentration. That even 1.5 per cent. sugar does not change the boundary movement has been proved by experiment.

Measurements.

The potential gradient employed was between 1 and 2 volts per cm.

The temperature in Section I. was 18.2° - 19.1° and, in Section II., 17.2° - 19.7° .

In the measurements of Section II. both rising and falling boundaries were observed; in Section I. only rising ones. The readings were made with the naked eye.

* The solubility is (according to K. Schick, *Z. physik. Chem.*, 1902, 42, 172) 0.41 gm./l. Two of my solutions contained 0.42 and 0.38 gm./l.

The mobility in unit field was calculated by the equation

$$u = \frac{lq\kappa}{it}$$

where l is the displacement of the boundary in t sec., i the current strength, q the section of the tube A, and κ the conductivity of the sols. Of these quantities, t , q and i can be measured with a far higher precision than l and κ . The gross displacement l was from 2 to 3 cm.; as the error of reading cannot be reduced to less than 0.04 cm. the relative error of l is at least 1 to 2 per cent. The relative error of κ is even larger when sols without added salt are investigated. To prove that the solutions remain unchanged during an experiment I determined their conductivity in a small conductivity cell both before and after the cataphoresis.

After the cataphoresis the contents of tubes A and B, excluding those of U and T, were used. In sols with about 0.01 N NH_4Cl the difference did not exceed 0.5 per cent.; with pure sols, however, the recovered fractions conducted considerably better than the original preparations. When the difference exceeded 5 per cent. the results were rejected. I did not attempt to reach a higher precision as my task was to improve, not the precision of the moving boundary method, but its reliability.

TABLE II.

NH_4Cl mol 1×10^{-3}	κ $\text{ohm}^{-1} \text{cm}^{-1} \times 10^{-4}$	u^A cm. sec. 10^{-4} per volt cm	u^B cm. sec. 10^{-4} per volt cm
(1) $\text{As}_2\text{S}_3 + \text{NH}_4\text{Cl}/\text{HCl} + \text{NH}_4\text{Cl}$.			
0	1.54	7.25	5.8
0.06	3.28	4.70	4.20
3.85	7.43	4.40	4.55
9.62	14.0	4.03	4.03
(2) $\text{HgS} + \text{As}_2\text{S}_3 + \text{NH}_4\text{Cl}/\text{HCl} + \text{NH}_4\text{Cl}$.			
0	1.34	5.97	3.65
0.06	3.12	5.33	4.79
3.85	7.91	4.35	4.57
9.62	13.5	3.52	3.60
(3) $\text{HgS} + \text{As}_2\text{S}_3 + \text{NH}_4\text{Cl}/\text{As}_2\text{S}_3 + \text{NH}_4\text{Cl}$.			
0	2.08	6.72	6.46
0.06	3.21	3.70	3.67
3.85	6.90	3.40	3.32
9.62	13.6	3.34	3.12

TABLE I.

Experiment.	T_a grams.	T_b grams.	u^\dagger cm./sec. $\times 10^{-4}$ per volt/cm.
1	0.0100	0.0086	4.18
3	0.0083	0.0092	3.49
4	0.0082	0.0086	3.25
5	0.0100	0.0091	3.04
6	0.0095	0.0092	3.38
Average	0.0092	0.0089	

Results.

Section I.—In Table I. the analytically measured transport (T_a) is compared with that calculated from the boundary displacement (T_b). The sols contained about 0.001 mol./l. NH_4Cl , the concentration of the As_2S_3 sol was 7.96-8.32 gm./l., of the $\text{HgS}-\text{As}_2\text{S}_3$ mixture 8.60-9.20 gm./l. u^\dagger is the velocity of the rising boundary in a unit field.

Section II.—I compared, at different NH_4Cl concentrations, the movement of the boundaries $\text{As}_2\text{S}_3 + \text{NH}_4\text{Cl}$ aq. against $\text{HCl} + \text{NH}_4\text{Cl}$ aq. and $\text{HgS} + \text{As}_2\text{S}_3 + \text{NH}_4\text{Cl}$ aq. against $\text{HCl} + \text{NH}_4\text{Cl}$ aq. (Table II.). The concentration of NH_4Cl in the sols and in the supernatant liquid was the same, while to the supernatant liquid as much HCl was added as was

required to make its conductivity equal to the conductivity of the sol + NH_4Cl . The rising boundary was mostly sharp, the falling boundary (its velocity being denoted by $u \downarrow$) diffuse, especially in the experiments without, or with only a little, NH_4Cl ; the figures for $u \downarrow$ reported in the tables refer to the "boundary" between the clear supernatant liquid and the transition layer; the "boundary" between the transition layer and the apparently unchanged sol usually moved faster.

Table II. (3) contains results obtained by the new method. The superiority of the "two sols boundary" is obvious. The figures for $u \uparrow$ and $u \downarrow$ are more consistent than in (1) and (2) so long as the NH_4Cl content is small. With much NH_4Cl the conductivity of the sol particles plays but a subordinate rôle and the difference between $u \uparrow$ and $u \downarrow$ becomes accidental and small in all cases.

Henry and Brittain¹ derived from the Kohlrausch-Weber theory that $u \uparrow > u \downarrow$ and $u \downarrow > u$, when u denotes the true mobility, and both $u \uparrow$ and $u \downarrow$ are determined with an ionic supernatant liquid the ions of which liquid move faster than the colloid particles. This conclusion, made for true mobilities, holds for most of the mobilities of Table II. (3).

Summary.

Experimental investigations have been made of an improved method of measuring cataphoresis based on the observing the movement of a boundary between two almost identical sols of different colours.

I am indebted to Mr. D. C. Henry for hospitality and help and to the Professional Committee for German Jewish Refugees for a maintenance grant.

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REVIEWS OF BOOKS.

Atomtheorie. By A. HAAS. Berlin: Walter de Gruyter & Co. Pp. viii and 292. Price R.M. 8.50 and R.M. 10.

This work is too well known to need detailed description. In this, the third, and very much enlarged edition, the author makes a gallant effort to keep his readers informed of the latest developments in the breathless story of atomic physics. The seven sections of the book deal with, *Elektronen, Atome und Lichtquanten; die Grundlagen der Atommechanik; die Spektren der Atome; die Röntgenstrahlen; die Atomkerne; die Molekeln; die Wechselwirkung zwischen Licht u. Materie.*

The treatment is throughout strictly elementary, and marked with those qualities of precision, clarity and distinction which are associated with the name of the author.

It may be remembered that a generation ago, an effort was made to present the Spencerian philosophy in compressed form by applying a footnote to Spencer's voluminous pages, and compressing the contents of each page to one-tenth of its original value.

Professor Haas's book is presented in seven chapters and sixty-six subsections. Not the least interesting feature of the book is an appendix of some sixteen pages, in which, in sixty-six paragraphs, corresponding

paragraph by paragraph with the sections of the full text, is given a complete and most helpful conspectus of the contents of the volume. Although this may be putting a premium on idleness, as doing for the student what he ought to do for himself, there is no denying the usefulness of such an appendix.

The simplicity and clarity of the exposition are a measure of the care and thought which has gone to the writing of a volume which may be unreservedly recommended to the university student.

A. F.

Annual Reports on the Progress of Chemistry, Vol. XXXII FOR 1935.
(London : The Chemical Society. Pp. xiii and 527. Price 7s. 6d. net.)

The amount of material reported this year which bears directly on work with which the Faraday Society is concerned is greater than ever. Special mention may be made of the following reports : Radioactivity and sub-atomic phenomena (H. J. J. Braddick), Isotopes (S. Glasstone), Spectroscopy (G. B. B. M. Sutherland), Determination of thermodynamic constants (Glasstone), Chemical Kinetics (E.A. Moelwyn-Hughes), Surface chemistry (E. B. Maxted), Physical basis of optical rotatory power (G. B. Allsop), Dipole moment, and valency angles (Glasstone), Non-ferrous alloy systems (E. S. Hedges), Crystal physics and crystal chemistry (J. D. Bernal), Properties of real crystals (Bernal), Molecular crystals (D. M. Crowfoot), Polymerisation (E. H. Farmer).

These reports, however, by no means exhaust the interest of the physical chemist. Moreover, the volume provides the usual admirable survey of work in those allied branches of the science into which the influence of the physical chemist and of the chemical physicist is more and more penetrating.

Die Umwandlungen der chemischen Elemente. By ARTHUR HAAS
(Walter de Gruyter and Co. 118 pages and 31 figures.

This little book gives a vivid account of recent work on the new subject of nuclear physics and chemistry. It commences with a survey of the properties of radiation and of stable atomic species which is followed by a discussion of the methods used to disintegrate nuclei. The results of disintegration experiments are then considered and a final chapter is devoted to artificial radioactivity.

The subject is treated descriptively and without mathematics but numerous diagrams and photographs add greatly to the value of the book. No less than nineteen photographs of cloud chamber tracks are provided and give striking demonstrations of such phenomena as the production of positrons, the disintegration of lithium by protons and deuterons and many other atomic disruptions.

S. S.

Allgemeine Photochemie. By J. PLOTNIKOW. Second Edition, revised and enlarged. 909 pp., with 218 Figures. (Walter de Gruyter & Co., Berlin and Leipzig, 1936. Price RM 28.50 ; bound RM 30.)

This edition bears practically no relation to the first (1910) although it contains a description of most of the early work in Photochemistry. The author has described a large amount of work other than his own, but

has included very few of the modern theories. The book is most comprehensive, particularly in the field of applied photochemistry, and contains a large number of references not given in other text-books on this subject; several of these were found, however, to be incorrectly given. The author concludes his book by a list of his 215 contributions to the scientific literature.

C. F. G.

Kolloidik. By A. VON BUZAGH. (Dresden, Theodor Steinkopff. Pp. xii + 323. Price RM. 15.)

The subtitle of this work describes it as "An Introduction to the Problems of Modern Colloid Science," while the title itself is stated to be a term coined by Professor Spiro to cover both colloid chemistry and colloid physics. The conservative reader will probably consider it unnecessary and will have the same feeling about a good deal of the exuberant nomenclature applied to a number of stereometric objects and relations.

They occur in the first chapters, devoted to the definition and classification of disperse and "difform" systems, the fundamental characteristic of which is periodic discontinuities in one or more properties. After discussing them, the author proceeds to give what he calls "the most general definition of the colloidal state" as follows: "Colloidal discontinuities are such spatial discontinuous alterations of properties as are coupled with continuities of the order of magnitude between the wave-length of light ($500\text{ m}\mu$) and the average molecular size ($1\text{ m}\mu$). Systems with this structure are described as colloidal systems. Modern "kolloidik" is the science—the physics and chemistry—of 'colloidal discontinuities.'" He supports this definition by showing that a number of "dispersity functions," *i.e.* formulæ for certain properties containing the particle radii as independent variable, pass through maxima or minima, or show a greatly increased rate of change, when the radius falls within the colloidal range. Whether the validity of general laws in the colloidal range is really a reason for what the author calls "The autonomous way of regarding colloids" seems doubtful on etymological grounds, apart from other objections to these political metaphors. In trying to prove here and elsewhere that colloid science is to be considered a separate discipline the author is flogging a dead horse; the enormous bulk of material makes such a course inevitable for practical reasons.

What has been said above covers the contents of the first four chapters. The fifth, entitled "The morphology of disperse and difform systems" is for the greater part still concerned with the formulation and classification of largely ideal configurations. The contents of the remaining chapters are: VI, Aggregates (Primary); VII, Aggregates (Secondary); VIII, Phenomena at Interfaces (Adsorption); IX, Phenomena at Interfaces (Electrical Properties of disperse systems); X, Changes of State of Colloids (Genesis of colloidal solutions); XI, Changes of State (The Destruction of Colloidal Solutions); XII, (Internal Changes of State in Colloids).

The last five chapters, which contain substantially what the reader expects to find in a text-book of colloid science, cover 120 pages, or somewhat less than half the text. The author throughout insists on the difference between physical boundary zones and geometrical interfaces, which

leads him to reject the "chemical" theories of adsorption and of the electric charge on particles. Such criticisms are always expressed with fairness and urbanity. Perhaps the author's avowed intention to write something more than a text-book accounts for the disproportion between the space devoted to this section and that of 77 pages covered by the two chapters on "Aggregates," which attempt to give a general survey of the structure of matter.

It is this tendency, apparent throughout the work, of beginning very much at the beginning, which makes one feel somewhat uncertain as to the class of readers for whom the book is intended. It is hardly suitable for those approaching the subject for the first time, but will be of interest to those possessing a reasonable knowledge of it as the first complete and consistent statement of the views of the Leipzig school of colloid science. Since this is at present the only school left in Germany, this interest may well become an historical one in the future.

E. H.

Physical Aspects of Organic Chemistry. By W. A. WATERS, M.A., Ph.D. George Routledge and Sons, Ltd. Pp. xv + 501. 25s. net.

This valuable book deals with the developments in organic chemistry which have arisen from modern theories of valency and electronic theories of organic reactions. The main theme is the existence of two types of chemical bond, polar and non-polar, and the classification of reactions into two corresponding groups which involve ions and free radicals respectively. A wide range of chemical theories is surveyed, usually from the historical standpoint and the treatment is vivid and interesting. The chapters on hydrolysis, on molecular rearrangements, and on aromatic reactions are particularly valuable and give a well-arranged and fully documented introduction to modern work on these subjects.

The book was originally planned in collaboration with Professor T. M. Lowry who contributes an introduction. The views of the Cambridge School naturally receive special attention but are not unduly emphasised, and the author is to be congratulated on a well-balanced account of modern theories of organic chemistry.

S. S.

A Text-book of Organic Chemistry (Schmidt). Third English Edition. By H. GORDON RULE. London: Gurney & Jackson, 1936. Pp. xxiv and 865. Price 25s. net.

The previous editions were reviewed in these *Transactions* (22, 108, and 28, 662). There has been no intervening German edition, so that the judicious and critical additions (and no less careful deletions to ensure, nevertheless, an increase of only 22 pages in size) are due entirely to Dr. Rule. The text has been carefully revised and the constant references to work between 1932 and 1935 provide sufficient evidence that here is a text-book which definitely does not warrant the oft-heard criticism that new work does not find its way into text-books for at least ten years.

It is perhaps from the introductory 98 pages that the physical chemist will judge the volume; recent work, for instance, on stereochemistry and dipole moments is adequately summarised. Later sections deal with other

matters which have recently exercised this Society, *e.g.*, the molecular structure of starch and the constitution of cellulose. There is a new section devoted to vitamins and hormones.

The production is excellent; the judicious use of clarendon type in the text, in particular, enables speedy reference from index to text.

The Thermochemistry of the Chemical Substances. F. R. BICHOWSKY and F. D. ROSSINI. (Reinhold Publishing Corp. N.Y., 1936. 35s.) (Chapman and Hall, Ltd., London.)

This book contains self-consistent "best values" of the heats of formation of all chemical substances which have been measured, except organic compounds having more than two carbon atoms. The list includes heat values from spectroscopic data for excited states and unstable molecules, but no values for deuterium compounds appear. It is a recalculation and extension of the data presented in the International Critical Tables, and as a book of reference is a necessity for a scientific library. The authors have arranged the tables in a very precise and simple form, and in a separate section give a brief critical survey of the experimental work relating to each substance. It is no fault of the book, but a reflection on the trend of experimental science, that a vast number of the results are derived from the work of Thomsen and Berthelot now fifty or so years old. To quote the preface: "The authors have been reluctant not to use the almost universally accepted standard temperature of 25° C. for thermodynamic calculations; but the selection of 18° as the standard temperature is practically necessary in this case because all of the monumental work of Julius Thomsen and of Marcellin Berthelot was done at or near 18°, and there are not now available sufficient heat capacity data with which to make accurate conversion to 25°." The following typical notes on the data of some common substances are significant: "HCN (g). The data on the heat of combustion are: Thomsen (before 1886) 158.5; Berthelot (1881) 159.3. CS₂. Thomsen (before 1886) measured the heat of combustion of gaseous carbon disulphide, and Berthelot (1881, 1893) that of the liquid." The references to work on formic acid are dated 1852 and 1886 for the vapour, and 1873 to 1892 for the liquid. About fifteen years ago the subject of accurate calorimetry was taken up by a number of contributors to the Journal of the American Chemical Society, but the elaborate machines constructed were not used for any extensive revision of the older results, except for the work now being carried out by Rossini on organic compounds.

E. J. B.



THOMAS MARTIN LOWRY

THOMAS MARTIN LOWRY, C.B.E., F.R.S.

(1874 to 1936).

THE FARADAY SOCIETY mourns the loss of Professor T. Martin Lowry, one of its distinguished Past-Presidents.

This memoir speaks only of his work for the Faraday Society. He watched and guided its progress with a keen personal pride and thus helped to contribute much to the sum of human knowledge. This work we gratefully record; others may speak of the work of his laboratory which is to be found not only in the pages of these *Transactions* but in many other journals.

Dr. T. Martin Lowry was a founder-member of the Society and from its very early days took an active interest in the organisation of its activities. The Society's early records show that he was an auditor in 1905 and became a member of Council in 1906. This Council, on the 27th November, 1906, decided that steps should be taken to bring into the new Society more of those who were engaged in pure physical chemistry. As one means to this end the Earl of Berkeley was invited to show his experiments on Osmotic Pressure. From this simple invitation there arose a meeting, held on 29th January, 1907, at which papers were read not only by Berkeley but also by Lowry, Dampier-Whetham and Kahlenberg (of Wisconsin). The papers and the discussion were reported together, under the title of a "General Discussion on Osmotic Pressure." In May, 1907, the success of this meeting warranted the organisation of another "General Discussion" on the subject of "Hydration," which was organised by Lowry and the secretary (F. S. Spiers), and took place in June, 1907.

Thus Lowry laid the foundations of a policy on which the success of this Society has largely been based; he realised the value of specialised discussion of a topic limited in scope but of general interest and, nearly 30 years ago, appreciated the importance of inviting distinguished overseas workers to co-operate. The reputation of these "General Discussions," organised along the lines laid down in early 1907, grew to such an extent that when, after almost continuous service to the Society in one capacity or another, Lowry was, in 1928, elected President, he had the privilege of welcoming many distinguished workers who had travelled the seven seas to meet together under his Presidency.

Members of this Society will long remember him, not only for his part in the growth of the Society, but also as their host on the many occasions when, as Professor of Physical Chemistry, he welcomed the Society to Cambridge. It was fitting that Lowry should have been President during the 25th Jubilee year of the Society and that the (50th) "General Discussion," that on Free Radicals, should have been held in his laboratory.

DIAMAGNETIC SUSCEPTIBILITY OF THALLIUM COMPOUNDS.

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Part I. Thallous Compounds

A study of the literature dealing with the magnetic properties of the chemical elements reveals that very little systematic study has been made of a wide range of compounds of one chemical element. The work of Ikenmeyer¹ on the magnetic susceptibilities of the alkali metal halides only covers one type of compound. Sugden,² in 1934, investigated a range of silver and copper compounds, and Spencer and Hollens³ the compounds of cadmium, but these represent practically the only systematic investigations in this field.

In the present paper the diamagnetic susceptibilities of some thirty thallous salts have been measured, covering a wide range of compounds. From the molar susceptibilities of the salts, the gram ionic susceptibility of the thallous ion has been calculated, and the value compared with the theoretical one obtained from Slater's approximate wave functions. Values of the average mean square radius, and the radius of the outer orbit of the thallous ion have been deduced from the experimental data and are compared with the corresponding values from theory.

Experimental.

Preparation of Compounds.

A good commercial specimen of thallous carbonate (99.95 per cent. pure) was used as starting material and was tested for ferromagnetic impurities, *e.g.*, iron, nickel, and cobalt, by B.D.H. spot tests and gave negative or negligible results. Lead was also tested for and found absent. The compounds measured were prepared and purified by the usual methods from A.R. materials. All acids used were tested and shown to be free from iron. In a few cases special methods were necessary to obtain a pure specimen. Thallous bromate prepared by addition of bromic acid to thallous carbonate resulted in an impure product, which even after recrystallisation contained an appreciable amount of thallic bromate as impurity. A pure specimen was obtained by addition of A.R. potassium bromate to pure recrystallised thallous nitrate, thallous bromate being precipitated. A pure specimen of the sulphite could not be prepared by double decomposition of thallous sulphate and sodium sulphite, but was obtained from a solution of the hydroxide, which was first saturated with sulphur dioxide to form the bisulphite. By addition of an equivalent amount of thallous hydroxide solution to this, crystals of the normal sulphite were obtained, on careful evaporation. Attempts to prepare

¹ Ikenmeyer, *Ann. Physik*, 1929, 169.

² Sugden, *J.C.S.*, 1932, 161.

³ Spencer and Hollens, *J.C.S.*, 1935, 495.

the permanganate by Meyer's method⁴ proved unsuccessful, oxidation of the thalious compound to thallic oxide resulting in every case, even at low temperatures.

Analysis.

The purity of the compounds prepared was determined by the tests for ferromagnetic impurities, and by estimation of the thallium content of the compound. Thallium was estimated as chromate, the method being previously tested with a pure recrystallised specimen of thalious sulphate and was found to give consistent results with an error of less than 0.1 per cent. under the following conditions: To 0.3-0.4 gm. of the thallium salt, dissolved in 200 c.c. of water, and made alkaline with a few drops of ammonia, 2 gms. of solid A.R. potassium chromate were added at the boiling-point. The precipitate was stirred until complete coagulation resulted, cooled, allowed to stand for 12 hours, and filtered cold through a sintered glass crucible. The precipitate was washed with 50 c.c. of 1 per cent. potassium chromate solution, and 100-150 c.c. of 50 per cent. alcohol, which was found to be the amount necessary in most cases to wash free from other ions. The precipitate was then dried at 120° and weighed.

It was found necessary to keep strictly to the above conditions as variable results were obtained with more dilute or concentrated solutions, or on washing with water alone. Any compound giving a thallium content differing by more than 0.2 per cent. from the theoretical value was recrystallised.

Measurement of Susceptibility.

The mass susceptibility was measured by a modified Gouy method as previously described,⁶ at atmospheric temperature. Six closely agreeing measurements, each the mean of three readings, were made on the solid salt with fresh packings of substance in each case. The maximum deviation from the mean value was never greater than 2 per cent. and in most cases of the order 1 per cent.

Results.

In Table I. results are tabulated in three groups, in order of increasing number of electrons N , the first consisting of salts of thallium with univalent negative ions, the second with divalent and trivalent ions; and the third of organic salts. The mean experimental magnetic mass susceptibility χ is recorded in column 3, for each compound, and the molar susceptibility, $\chi_M = \chi \times M$ in column 4. Column 5 gives values of δ representing the ionic susceptibility of the negative ion which must be subtracted from the molar susceptibility to give the ionic susceptibility of the thalious ion. This method of determining the ionic susceptibility assumes that the salts are polar, and that the molar susceptibility is made up of the sum of the ionic susceptibilities. The values of δ in the first two groups are taken from the International Critical Tables VI., p. 349, except those marked (a) which are due to Sugden,² and (b) which were specially determined, as described below, no values being given in the literature. In these latter cases the susceptibility of the corresponding potassium salt was measured and the value for the negative ion calculated from the known value for the potassium ion. The experimental results so obtained are shown in Table II. The values of δ for the organic salts were obtained from Pascal's values for atoms and linkages. In addition, the value for the nitrite ion was obtained by calculation from the

⁴ Meyer and Best, *Z. anorg. chem.*, 1899, 169.

⁶ Trew and Watkins, *Trans. Faraday Soc.*, 1933, 1310.

TABLE I.

	Substance.	N.	$-10^6 \chi$.	$-10^6 \chi_M$.	δ (Negative).	$-10^6 \chi_A$ Thallium Ion.
GROUP I.: <i>Univalent Anions.</i>	TiF	90	0.201	44.4	6.3	38.1
	TiCN	94	0.212	49.0	10.8	38.2
	TiCl	98	0.241	57.8	20.1	37.8
	TiCNO	102	0.225	55.5	16.2	39.3
	TiNO ₂	104	0.203	50.8	13.4	37.3
	TiCNs	110	0.254	66.7	30.0 ^a	36.7
	TiNO ₂	112	0.212	56.5	18.0	38.5
	TiBr	116	0.225	63.9	30.6	33.3
	TiClO ₂	122	0.228	65.5	26.0 ^{a,b}	39.5
	TiClO ₄	130	0.238	72.5	29.6 ^b	42.9
	TiI	134	0.248	82.2	44.6	37.5
	TiBrO ₂	140	0.229	75.9	35.6 ^b	40.3
	TiHO ₂	158	0.229	86.8	47.4 ^b	39.4
					Mean value	38.4
GROUP II.: <i>Divalent and Tervalent Anions.</i>	Ti ₂ S	178	0.202	88.8	15.0	36.9
	Ti ₂ CO ₃	192	0.217	101.7	28.0	36.9
	Ti ₂ SO ₃	202	0.203	99.3	22.3	38.5
	Ti ₂ SO ₄	210	0.223	112.6	37.0 ^a	37.8
	Ti ₂ CrO ₄	218	0.075	39.3	+35.2 ¹ +33.0 ^{1b}	36.7
	Ti ₂ PO ₄	290	0.205	145.2	35.4	36.6
	Thallous alum	620	0.416	532.1	456.5 ^b	38.3
					Mean Value	37.4
GROUP III.: <i>Organic Anions.</i>	Formate	104	0.220	55.0	16.9	38.1
	Acetate	112	0.262	69.0	30.0 ^a	39.0
	Benzoate	144	0.349	113.5	66.1	47.4
	Tartrate	158	0.304	107.4	63.8	43.6
	Oxalate	206	0.220	109.4	27.9	40.7
	Malonate	214	0.240	122.6	39.8	41.4
	Citrate (+1 H ₂ O)	330	0.274	224.8	92.1	44.2
					Mean Value	42.1

nitrate ion, the chromate similarly from the dichromate, and the carbonate by the same method as the organic salts. Column 6, Table I., shows χ_A the resulting atomic susceptibility of the thallous ion.

Discussion of Results.

The molar diamagnetic susceptibility of a polar salt in the solid state may, in general, be regarded as the sum of the susceptibilities of the positive and negative ions. For a mononuclear spherically symmetrical atom or ion this is given by Langevin's equation:—

$$\chi_A = -\frac{e^2 L}{6mc^2} \Sigma \bar{r}^2 = -2.83 \times 10^{10} \Sigma \bar{r}^2$$

where $\Sigma \bar{r}^2$ on the classical theory is the mean square radius summed for all the electrons in the atom or ion, or on the newer quantum mechanical view is the square of the average effective electron density distribution.

In solid crystals the interionic distances depend on the ionic radii and hence the factors which determine such distances in a crystal must to a large extent influence the susceptibility. The ionic radius, or outer electron density distribution of an ion is limited in a crystal by adjacent ions, so that the radii of such ions, together with the diamagnetic susceptibility (to which the outer shell of electrons contributes by far the largest amount), should be less than that of the free ion, or the ion in solution.

TABLE II.—POTASSIUM SALTS.

 δ K-ion = -18.5×10^{-6} (I.C.T.).

Substance.	$-10^6 \chi$	$-10^6 \chi_M$	$-10^6 \chi_A$ Negative Ion.
KClO ₃	0.361	44.3	25.8
KClO ₄	0.347	48.1	29.6
KBrO ₃	0.324	54.1	35.6
KIO ₃	0.308	65.9	47.4
K ₂ CrO ₄	0.020	4.0	+33.0
Potash alum *	0.520	493.5	456.5

* This value is taken from unpublished work by G. T. Oddie (Sister Mary Cecilia) working in this Laboratory.

Furthermore, Goldschmidt ⁶ has shown that the ionic radius is modified by the co-ordination number of the ion (*i.e.*, the number of ions of opposite sign surrounding the ion in question) as also by the nature and size of such ions. The interionic distance has been shown to decrease with a diminution of the co-ordination number by an amount of the order 3.8 per cent. Similar variations in atomic diamagnetic susceptibility would be expected to follow. In particular, since the number of ions of opposite sign (and hence the co-ordination number), surrounding a given ion is less in its salts with divalent ions than with univalent ions, the diamagnetic susceptibility might be expected to be lower in the former case. The results in Table I. show that for the thallous ion the mean ionic susceptibility as determined from the salts with divalent and trivalent anions is -37.4×10^{-6} , while the value from the salts with univalent anions is -38.4×10^{-6} , in exact accord with Goldschmidt's observations on change of ionic radius with co-ordination number. Allowing for the fact that the salts investigated are not all of the same type, it is striking that this decrease is of the same order (about 3 per cent.) as that found by Goldschmidt.

In the case of the organic salts, it will be noted that while the simple salts give a value for the atomic susceptibility of the thallous ion in agreement with that derived from the salts with univalent anions, the salts with larger organic molecules give a very much higher value. This becomes very evident if these salts are rearranged in order of increasing number of carbon atoms in the molecule, when it will be seen that, roughly, the value of the ionic susceptibility increases with the number of carbon atoms. It should be noted that this increase is not due to any bond effects within the anion, as these have been included in calculating δ for the organic anion by Pascal's method. It appears, therefore, that the increase in size of the negative ions surrounding the thallous ion results in an increase in the effective ionic radius and hence of the susceptibility of that ion. The organic anion thus appears to have a "diluting" effect on the charge surrounding the thallous ion, and so raises its ionic susceptibility to a value nearer to that of a free ion.

⁶ Goldschmidt, *Trans. Faraday Soc.*, 1929, 253.

The results in Table I. have been arranged in order of increasing number of electrons within the molecule and it will be seen that there is, on the whole, a linear increase of molar susceptibility with increasing number of electrons, although certain very marked deviations do occur. In particular, the values for the chloride, thiocyanate and iodide are considerably higher than the average. Salts with anions of similar constitution, *e.g.*, nitrate, chlorate, bromate, and iodate, form a definite linear sequence. Ikenmeyer,¹ has shown that an approximately linear relationship holds for the gram molar susceptibilities of the alkali halides, determined from measurements in solution, when the susceptibilities are plotted against number of electrons in the molecule. The susceptibility can be expressed in the form $\chi_M = c_1 N_m + c_2$ where N_m is the sum of the atomic numbers of the atoms in the molecule, or total number of electrons, c_1 is a general constant $= 0.803 \times 10^{-6}$ and c_2 a constant specific for a given series of salts. The molar susceptibilities of the thallous compounds in general agree with the same relationship, allowing for the much wider difference in types of compounds considered. For thallous salts, c_1 , the average increase in diamagnetism per electron is approximately 0.7×10^{-6} (agreeing reasonably well with Ikenmeyer's value) while c_2 has an average value of -17×10^{-6} becoming lower by about five units for the chloride, acetate, thiocyanate and iodide, and similarly higher for the nitrate series of ions. The relation holds for the divalent and univalent anions if one-half and one-third of N and χ_M are used respectively. The citrate, benzoate and tartrate are again exceptional. These and the other deviations from linearity are probably due to the cause already discussed, namely, specific effects due to the crystalline form of the compounds investigated.

Comparison of Theoretical and Experimental Susceptibilities.

The values of Σf^2 in the Langevin formula have been evaluated for the different electron groups in atoms and ions, by Pauling⁷ from quantum mechanics, by Hartree⁸ using a self-consistent field method of determining the radial charge distribution, and by Slater⁹ from wave mechanics using an approximate solution of the wave equation of an electron. Brindley¹⁰ has shown that the Slater method gives results in best agreement with experimental susceptibilities for most atoms and ions, and in particular, for those with the larger values of r to which class the thallous ion belongs. Slater's rules for determining the screening constants for the various electrons in an atom or ion have been applied to obtain a theoretical value for the susceptibility of the thallous ion. Using this method, for any electron

$$f^2 = \frac{(n')^3(n' + \frac{1}{2})(n' + 1)}{(Z - s)^2}$$

where n' is the effective principal quantum number and $Z - s$ the effective nuclear charge for each electron considered, Z being the atomic number and s the appropriate screening constant derived for any electron by considering the screening effects on it of other electrons in the atom, using Slater's rules. The susceptibility is obtained by

⁷ Pauling, *Proc. Roy. Soc.*, 1927, 181.

⁸ Hartree, *Proc. Camb. Phil. Soc.*, 1928, 111; *Proc. Roy. Soc.*, 1933, 141.

⁹ Slater, *Physic. Rev.*, 1930, 57.

¹⁰ Brindley, *Phil. Mag.*, 1931, 786.

summing over all the electrons in the ion. When \bar{r}^2 is expressed in atomic units (multiples of a_0 , the radius of the Bohr orbit in normal hydrogen = 0.528×10^{-8} cm.) then

$$\chi_A \times 10^6 = -2.83 \times 10^{10} (0.528 \times 10^{-8})^2 \cdot \sum \frac{(n')^2(n' + \frac{1}{2})(n' + 1)}{(Z - s)^2}$$

$$= -0.790 \sum \frac{(n')^2(n' + \frac{1}{2})(n' + 1)}{(Z - s)^2}.$$

The appropriate values for the thallous ion are shown in Table III. whence $-10^6 \chi_A = 79.99 \times 0.790 = 63.19$, the theoretical atomic susceptibility of the thallous ion.

It will be seen that the theoretical and experimental susceptibility values are of the same order of magnitude, but the experimental value is rather less than two-thirds of the theoretical value. The calculated value is that for the free ion, whereas the experimental value is derived from measurements on the crystalline solid, and therefore, as considered previously, may to some extent be lower due to interionic forces, but these effects should only cause a difference of some 3.8 per cent. A real discrepancy between experiment and theory is therefore indicated by the above results. This is supported by Brindley's results¹⁰ for a number of other atoms and ions. He has shown that there is an increasing divergence between theoretical and experimental susceptibilities with increasing atomic weight of the element concerned. This point will be further considered later.

Ionic Radius.

From the experimental atomic susceptibility the value of $\Sigma \bar{r}^2$ can be evaluated by means of the Langevin equation, giving for the thallous ion $\Sigma \bar{r}^2 = 48.49$ in atomic units, or 13.44×10^{-16} in absolute units. The value $\Sigma \bar{r}^2 = 48.49$ is to be compared with the value of 79.99 deduced from theory. This average mean square radius or effective electron density distribution is, of course, not the square of the outer radius, but a composite factor depending on all the extra-nuclear electrons in the ion. A value for the actual outer radius cannot be obtained directly from this since there is no direct means of determining the contributions of the various shells to this factor. Although the outer (6s) shell will contribute a large proportion of the susceptibility, Table III. shows that

TABLE III.—SCREENING CONSTANTS AND $\Sigma \bar{r}^2$ FOR THE THALLOUS ION.

$Z = 81$. Number of Electrons = 80.

Electron Groups.	s .	$Z - s$.	n' .	$\Sigma \bar{r}^2$.
1. s^2	0.30	80.70	1	0.00
2. s^2, p^6	4.15	76.85	2	0.04
3. s^2, p^6	11.25	69.75	3	0.21
3. d^{10}	21.15	59.85	3	0.35
4. s^2, p^6	27.75	53.25	3.7	0.76
4. d^{10}	39.15	41.85	3.7	1.54
4. f^{14}	52.30	28.70	3.7	4.59
5. s^2, p^6	57.65	23.35	4.0	5.28
5. d^{10}	71.15	9.85	4.0	37.12
6. s^2	75.65	5.35	4.2	30.10
			Total $\Sigma n' \bar{r}^2$	79.99

the 5d shell in the case of the thallous ion also contributes a large amount. By making use of the theoretical values in Table III. the radius of the outer shell can be estimated from the experimental susceptibility. Slater,⁹ has shown that the effective radial electron density (and hence a measure of the radius), of any shell is given by the formula $\bar{r}' = \frac{(n')^2}{(Z-s)}$.

Applying this to the 6s shell, with the appropriate value of $(Z-s)$, gives for the thallous ion the value \bar{r}' (theoretical) = 1.78 A.U. It has already been pointed out that the theoretical susceptibility is too high, therefore this value of the radius of the outer shell will be correspondingly too large. A value of \bar{r}' from experimental data may be estimated from the value of $\Sigma \bar{r}^2$ derived from the experimental susceptibility as follows:—

Since $\sqrt{\Sigma \bar{r}_e'^2} : \sqrt{\Sigma \bar{r}_i'^2} :: \bar{r}_e' : \bar{r}_i'$ (where \bar{r}_e' and \bar{r}_i' are the radii of the outer shell, or orbit, given by experimental and theoretical data respectively, and $\Sigma \bar{r}_e'^2$ and $\Sigma \bar{r}_i'^2$ are the corresponding average mean square radii)

then $\bar{r}_e' = \frac{\sqrt{48.49}}{\sqrt{79.99}} \times 1.78 = 1.38$ A.U.

Goldschmidt's value for the ionic radius of the thallous ion from X-ray data is 1.49, slightly higher than the value from the susceptibility data. Bearing in mind the uncertainty of the theory involved in estimating the value 1.38 from the experimental susceptibility, this may be taken to be in good agreement with Goldschmidt's value.

Slater Wave Functions and Ionic Susceptibilities.

Brindley¹⁰ has shown that Slater's wave functions can also be applied to estimate the proportion of the molar susceptibility of a compound that is contributed by the constituent ions when these are simple mono-nuclear systems. It is thus possible from the experimental molar susceptibilities of those thallous compounds with single anions to deduce a value for the ionic susceptibilities based on the theoretical deduction that these are proportional to the average mean square radii of the ions concerned, as follows:—

$$\chi_A(\text{Ti}') : \chi_M :: \Sigma \bar{r}^2(\text{Ti}') : \Sigma \bar{r}^2(\text{Ti}') + \Sigma \bar{r}^2_{\text{anion}}$$

$$\therefore \chi_A(\text{Ti}') = \frac{79.99 \times \chi_M}{79.99 + \Sigma \bar{r}^2_{\text{(anion)}}}$$

TABLE IV.—IONIC SUSCEPTIBILITIES.
Calculated by Brindley's Method from Experimental Data.

Compound.	$-10^6 \chi_M$ Measured.	$\Sigma \bar{r}^2_{\text{anion}}$ Calculated.	$-10^6 \chi_A$ Thallous Ion.	$-10^6 \chi_A$ Anion.
TlF	44.4	10.27	39.34	5.06
TlCl	57.8	31.95	41.30	16.5
TlBr	63.9	49.73	39.41	24.5
TlI	82.2	74.19	42.64	39.6
Tl ₂ S	88.8	27.17	37.99	12.8
		Mean Value .	40.14	

$\Sigma \bar{r}^2$ for Thallous ion calculated by Slater method = 79.99 in Atomic Units.

Table IV. shows the results obtained in this way for the six compounds of this type that were investigated. The values of $\Sigma\tilde{r}^2_{(\text{anion})}$ in column 3 are taken from Brindley's values in the case of the chloride, bromide and iodide ions, and have been calculated similarly for the fluoride and sulphide ions. The values in column 5 are given by:

$$\chi(\text{anion}) = \chi_M - \chi(\text{Ti}^{+}).$$

It will be noted that the average value $-10^6\chi_A = 40.14$ for the ionic susceptibility of the thalious ion, deduced in this way is somewhat higher than that from purely experimental data. Table V. shows

TABLE V.—COMPARATIVE VALUES.

Compound.	Thalious Ion — $10^6\chi_A$.		Anion — $10^6\chi_A$.				
	I	II	I	II	III	IV	V
Fluoride . . .	39.34	38.1	5.06	6.3	8.2	—	—
Chloride . . .	41.30	37.8	16.5	20.1	25.3	24.0	23.7
Bromide . . .	39.41	33.3	24.5	30.6	39.3	37.5	34.1
Iodide . . .	42.64	37.5	39.6	44.6	58.6	55.7	50.2
Sulphide . . .	37.99	36.9	12.8	15.0	—	—	—

Column I in each case shows values calculated in Table IV.

Column II in each case shows experimental values, from Table I.

Column III. (Purely theoretical values calculated from Slater's screening constants taken from Stoner, *Magnetism and Matter*, p. 271.)

Column IV. Experimental values representing average results for measurements on solid salts due to Brindley.¹⁰

Column V. Experimental values taken from experiments on solutions by Weiss.¹⁰

values for the atomic susceptibilities of the positive and negative ions collected together from various sources for comparative purposes. This table shows that application of the Slater rules to assess the relative contributions of the positive and negative ions to the molar susceptibility in thalious compounds gives higher values for the positive ion and lower values for the negative ions than any other method. This agrees with the previous evidence that the theoretical value of $\Sigma\tilde{r}^2$ and hence of the diamagnetic susceptibility of the thalious ion is too high, again suggesting a need for a modification of the theory.

TABLE VI.—VALUES OF $\Sigma\tilde{r}^2$ FOR THE VARIOUS SHELLS.

	6s ² .	5d ¹⁰ .	5s ² , p ⁶ .	4f ¹⁴ .	4d → 1s, p Inclusive.	Total $\Sigma\tilde{r}^2$.
Mercury . . .	45.55	45.97	5.76	4.93	3.05	105.3
Thallium . . .	30.10	37.12	5.28	4.59	2.90	80.0
Lead ⁺⁺ . . .	21.37	30.59	4.87	4.29	2.57	63.7

Further light as to where this modification must be applied is given by a consideration of the adjacent elements in the periodic table, namely, mercury and lead. Thus, unionised mercury and the thalious and plumbous ions are electronic isomers, containing identical electronic shells and differing only in atomic number. The theoretical values of

Σf^2 for mercury and the plumbous ion, calculated by Slater's method, are shown in Table VI. giving 83.18 and 50.31 respectively, for the atomic susceptibilities, expressed in the usual units (*i.e.* all values are multiplied by -10^6). The corresponding experimental values are 38.75 for mercury, calculated from Honda's value of 0.193 for the mass susceptibility of liquid mercury at room temperature, and 44.3 for the plumbous ion. This latter value has been calculated from the mass susceptibilities for plumbous compounds quoted in the International Critical Tables, VI., p. 357, applying the appropriate corrections for the negative ions as in Table I. Comparing these theoretical and experimental values with those for the thallous ion, namely 63.2 (theoretical) and 38.3 (experimental), it will be seen that the discrepancy between theory and experiment is greatest for the element of lowest atomic number, *i.e.*, mercury. Examination of the values of Σf^2 for these three elements (Tables III. and VI.), shows that the susceptibility is in all three cases predominantly due to the ten $5d$ and the two $6s$ electrons. It is apparent, therefore, that the Slater rules give too high a value for the contribution of these shells to the diamagnetic susceptibility. The experimental atomic susceptibility of the plumbous ion is probably slightly high due to the tendency to covalency in its compounds. If the compounds were strictly polar the value would probably be about 38.0, by comparison with the corresponding values for mercury and lead, since there should be a slight decrease in the ionic susceptibility caused by the increase of the atomic charge Z . Allowing for this, the difference between the values of the theoretical and experimental susceptibilities is of the order 45 units for mercury, 25 units for thallium and say 12 units, or thereabouts, for lead. These differences represent a series of the type $(a+b)^2$, $(a)^2$, $(a-b)^2$. In Slater's formula for the susceptibility the only squared factor is $(Z-s)$, which will vary in the above way on passing from mercury to lead. It may then be inferred that the discrepancy between experiment and theory lies in the value of s the screening constant in Slater's formula. Thus, for either or both of the $5d$ and $6s$ shells the screening constant is too high, and hence the effective atomic number $(Z-s)$ is too low. Owing to this factor being squared in the formula, the deviation between theory and experiment will appear most marked for the element of least atomic number, namely, mercury. Angus¹¹ has suggested a modification in the method of grouping the s and p electrons, giving a slightly different value of the screening constant for these electron groups. In the case of the thallous ion this was found to make a difference of only one or two units to the theoretical susceptibility since it does not affect the values of Σf^2 for the $5d$ and $6s$ shells. This, therefore, does not explain the discrepancy, and the results given for the experimental susceptibility of the thallous ion support Brindley's view, based on theoretical considerations, that Angus' method is not justifiable. Some other modification which will explain all the above points seems to be needed in the theory.

Summary.

1. The magnetic mass susceptibility of 27 thallous compounds has been determined and a mean value of -38.4×10^{-6} obtained, from the salts with univalent anions, for the ionic susceptibility of the thallous ion.

¹¹ Angus, *Proc. Roy. Soc.*, 1932, 569.

2. Salts with divalent and trivalent anions give a slightly lower value, and salts with organic anions a higher value, explained as due to alteration in the ionic radius with change in co-ordination number.
3. The mass susceptibility of a number of potassium salts has also been determined to obtain correcting constants for the anions.
4. The theoretical atomic susceptibility has been calculated from Slater's approximate wave functions and is compared with the experimental value, which is considerably lower, indicating a discrepancy between theory and experiment.
5. A value of the ionic radius 1.36 Å.U. has been deduced from the experimental atomic susceptibility and is compared with the value 1.49 Å.U. obtained from X-ray crystallography.
6. The Slater method as applied by Brindley has been used to determine the relative contributions of the positive and negative ions in the salts with single univalent anions and again indicates too high a theoretical value for the atomic susceptibility of the thallous ion.
7. Comparison of the atomic susceptibility of the thallous ion with those for mercury and the plumbous ion indicate that the discrepancy between theory and experiment is due to too high a value for the screening constants of the $5d$ and $6s$ levels, given by Slater's method.

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ON THE RATE DETERMINING STEP IN THE DIFFUSION OF HYDROGEN THROUGH PAL- LADIUM.

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The notion that hydrogen can diffuse through metals, especially through palladium, is not new. It was early recognized that in this diffusion, there are two different types of processes: one occurring on the gas-metal boundary, the other within the metal.

Wagner¹ showed that the laws governing the diffusion of hydrogen into palladium differ according to whether the process on the boundary or that inside the metal is the rate governing step. This question has also been discussed by Melville and Rideal² who, among other things, investigated experimentally the diffusion of hydrogen and deuterium through palladium. The novelty of the present investigation lies in the fact that it has proved possible to investigate simultaneously the processes occurring both on the boundary and inside the metal. The principle of the method is as follows:—

Take a palladium disc, one side of which is in contact with hydrogen at a certain pressure, the gas being removed continuously by pumping from the other side. In the stationary state the concentration of hydrogen in and on the disc can be represented by Fig. 1. From each cross-section in the disc there will be a diffusion in the forward direction

¹ C. Wagner, *Z. physik. Chem., A*, 1932, **159**, 459.

² H. W. Melville and E. K. Rideal, *Proc. Roy. Soc.*, 1935, **153**, 89, 103.

(i.e., towards the vacuum side) and also in the backward direction. The quantity usually measured in diffusion experiments is the net diffusion leaving the disc at the vacuum side (i.e. C). It is desirable to measure the backward diffusion (i.e. B) since obviously, its magnitude compared with the net diffusion is important in deciding which of the two reactions

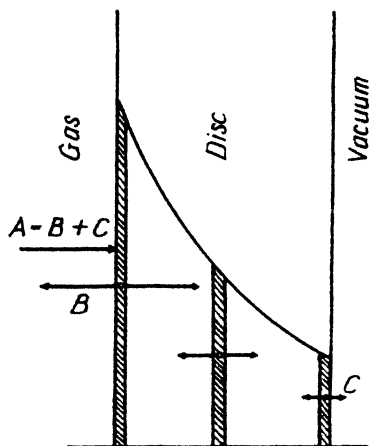


FIG. 1.—Concentration of hydrogen in a palladium disc in the diffusion process.

governs the rate of the diffusion through the metal; if it is very much larger than the net diffusion the reaction inside the metal is the slow process, whereas if it is comparable with the net diffusion the rate is then at least partly determined by the process at the boundary. The backward diffusion can be measured if parahydrogen (or orthodeuterium) is used instead of normal hydrogen for the diffusion experiments. In the reaction at the boundary every hydrogen molecule is dissociated (or at least the bond is sufficiently labile to ensure an *ortho-para*-conversion), and thus every molecule returning into the gas phase from the boundary layer by the process of back diffusion will be normal hydrogen and the rate of the *para*-conversion induced by the

metal surface can be used as a measure for the back diffusion. Since the *para*-conversion occurring in the gas phase and the amount of gas diffusing right through the metal can be measured simultaneously, from one single experiment carried out in this way, we can draw conclusions as to the mechanism of the diffusion process.

Experimental Arrangement.

Two series of experiments were carried out, one with a palladium disc and another with a palladium tube. The palladium disc (*cf.* Melville and Rideal²) (10 mm in diameter, 0.1 mm. thick) was welded to a platinum ring which in turn was sealed into a glass tube. Both the disc and the tube (10 cms. long, 2 mm. in diameter, 0.1 mm. wall) were used in the same arrangement as by Melville and Rideal. The disc was used in a horizontal position. The rate of diffusion was determined by measuring the decrease of the pressure by a Bourdon gauge. The *ortho-para*-conversion was followed by extracting small samples and determining the concentration by the usual microconductivity method.³ By suitable connections the diffusion from either the disc or the tube could be investigated by admitting the gas alternately to the two sides. The *ortho-para*-conversion on both sides of the disc or tube could be investigated in the same way. The separate investigation of both sides, though giving the same results so far as diffusion is concerned, was important for studying the reactions at the boundary.

The palladium tube or disc was heated in a small electric furnace, the temperature being measured by a thermometer. Two U-tubes kept at liquid-air temperatures prevented the palladium from coming into contact with grease and mercury vapour.

In all diffusion experiments particular care was taken that the stationary

² A. Farkas, *Z. physik. Chem., B.*, 1933, 22, 344.

state was actually obtained, *i.e.* the palladium was saturated with hydrogen. To ensure this, in most experiments (especially at lower temperatures) the palladium was first saturated, by leaving it in contact with hydrogen from both sides until no change of pressure was noticeable. Then the gas was rapidly pumped off from one side and the progress of diffusion measured. In these experiments the rate of the *para*-conversion was determined in a parallel run.

Since the volume of the connections was comparable with that of the tube containing the palladium care was also taken to ascertain that the rate of the *ortho-para*-hydrogen conversion should not appear to be reduced by insufficiently rapid diffusion between the palladium and the sampling tap.

Experimental Results with the Disc.

The progress of the diffusion of hydrogen through the palladium disc is shown graphically in Fig. 2, the square root of the pressure being plotted against time. In the pressure region investigated the amount of gas diffusing is proportional to the square root of the pressure.

The *para*-conversion proceeded strictly according to the formula

$$u_t = u_0 e^{-kt}$$

u_t and u_0 denoting the excess concentration of *para*-hydrogen at time t and $t = 0$ and k a constant.

For the sake of comparison we will characterise

FIG. 2.—Diffusion of hydrogen through a palladium disc (original state). The numbers in the circles denote the numbers of the experiments.

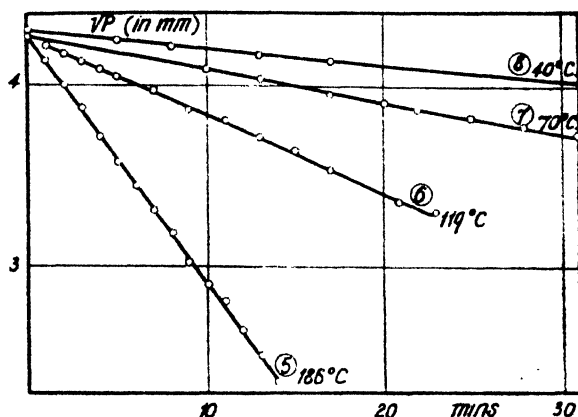


TABLE I.

No.	Temperature °C.	Half-life for Diffusion in Minutes.	Half-life for Conversion in Minutes.	
			On the Upper Side.	On the Lower Side.
5	186	9	—	—
13	130	—	6.3	—
14	130	25	—	—
6	119	28	—	—
7	70	68	—	—
12	68	—	30	—
8	38	138	—	—
11	24	—	100	2.4
22	— 29	—	—	6.5

the rate of diffusion and conversion of *parahydrogen* by their respective half-life periods, *i.e.* the time in which the pressure has decreased from say 20 mm. to 10 mm. Hg inside the diffusion vessel or in which half of the *parahydrogen* has been converted into normal. The half-life periods for the diffusion rate were taken from figures like Fig. 2.

Table I. shows the half-life periods

for the diffusion and conversion rates.

These results reveal that the rate of the *para*-hydrogen conversion is :

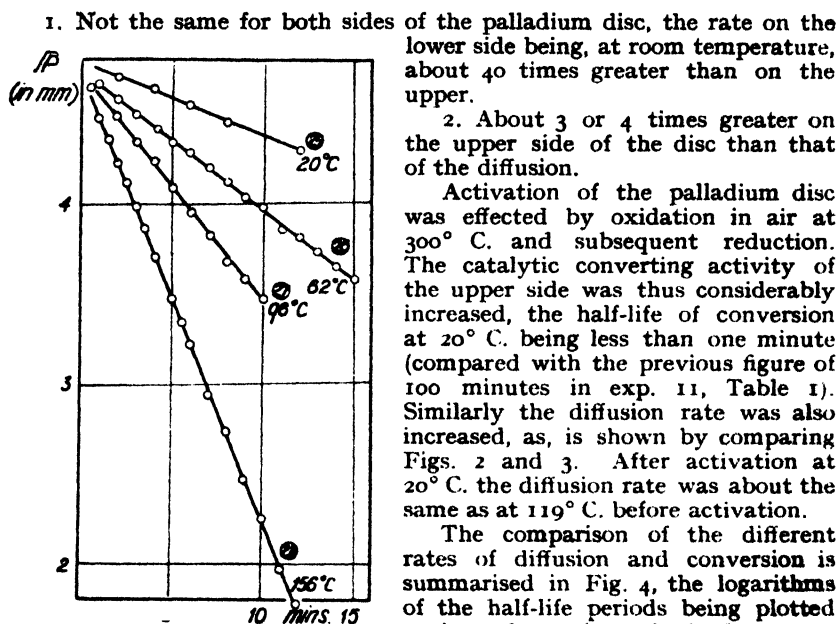


FIG. 3. — Diffusion of hydrogen through the palladium disc after oxidation and successive reduction.

lower side of the palladium disc before the activation, and curve IV to the diffusion rate after the activation. A close connection between the diffu-

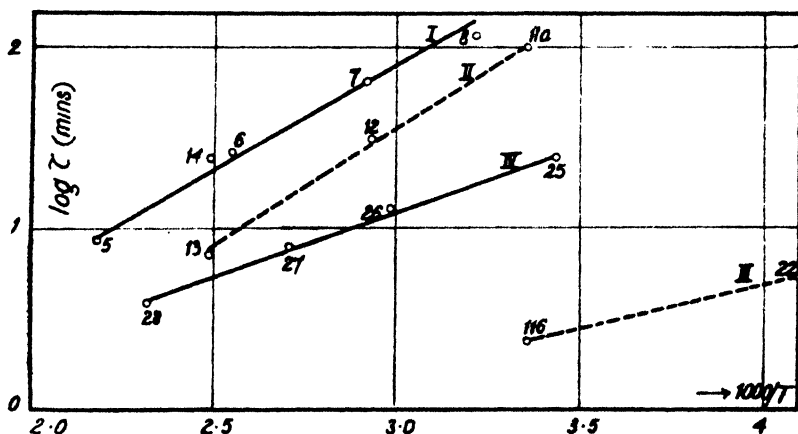


FIG. 4.—The rate of diffusion and *ortho-para*-conversion in dependence of temperature. Disc in original state:—

I = rate of diffusion, energy of activation 5.4 Kcals.

II = rate of conversion on the upper side of the disc, energy of activation 5.8 Kcals.

III = rate of conversion on the lower side, energy of activation 2.3 Kcals.

After oxidation and reduction:

IV = rate of diffusion, energy of activation 3.1 Kcals.

sion through the unactivated disc and the conversion on its upper side, will again be observed, the corresponding curves I and II being nearly

parallel and indicating similar energies of activation namely 5.4 Kcals. for the diffusion and 5.8 Kcals. for the *para*-H₂ conversion. The energies of activation (A) were obtained from the dependence of the half-life period (τ) on temperature according to the formula

$$\frac{d \log \tau}{dT} = - \frac{A}{RT^2}$$

On the other hand, curve III, characterising the conversion on the lower side, has a much smaller slope than I and II, showing that the activation energy for the conversion or dissociation of hydrogen on this side is much slower than on the other, namely 2.3 Kcals. Similarly the slope of IV, indicating the diffusion rate after the activation, is smaller than that of I, showing that after the activation the energy of activation has decreased from the original 5.4 Kcals. to 3.1 Kcals.

Experimental Results with the Tube.

Experiments performed with the palladium tube confirmed essentially the results obtained from the experiments with the palladium disc.

In the first series of experiments the tube was used after having been degassed at 350° C. but without any other treatment. The results are

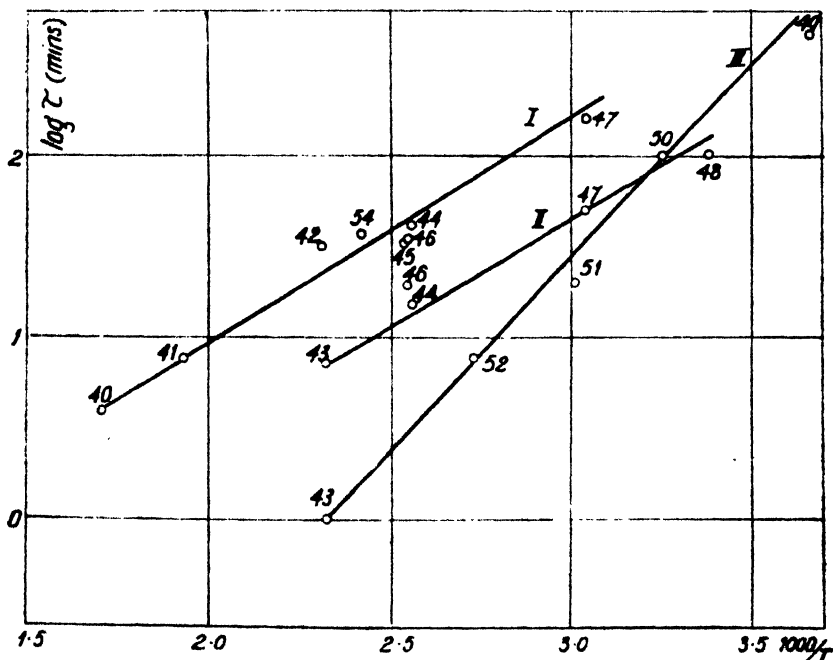


FIG. 5.—The rate of diffusion and of *ortho-para*-conversion in dependence of temperature. Tube in original state :

I = rate of diffusion, energy of activation 5.6 Kcals.

II = rate of conversion on inner side, energy of activation 5.4 Kcals.

III = rate of conversion on outer side, energy of activation 9.6 Kcals.

summarised in Fig. 5 the logarithm of the half-life periods for the diffusion, for the conversion on the inner and on the outer side of the palladium tube being characterised by the curves I, II and III respectively. Each point marked on the figure was again obtained from Figs. like 2 and 3. It will be noticed that the diffusion rate goes parallel with the rate of conversion

on the inner side of the tube, the latter rate being again 3 to 4 times faster.

The crossing of curves II and III at about 40° C is remarkable: above this temperature the conversion is faster on the outer side of the tube. This is due to the fact that the rate of conversion (or in general any heterogeneous reaction) depends on an energy of activation and on the magnitude of the surface available for catalysis. A hindrance of the reaction rate by a high energy of activation can be compensated by a large surface area and vice versa. The slope of the steeper line corresponds to an energy of activation of 9.6 Kcals., that of the other to an energy of 5.4 Kcals. Since this difference in the energies of activation would at 40° C make the conversion proceed $e^{-\frac{4200}{813R}} = 1000$ times more slowly, there must be a correspondingly larger area available on the outer surface to bring about a conversion rate equal on both sides.

The rates for the diffusion and conversion were quite reproducible as is seen by comparing Figs. 5 and 6. The results of the experiments summarised in curves I (diffusion) and II (conversion on the inside) do not differ appreciably from those contained in Fig. 5, although there was an interval of several days between the two series of experiments.

On the other hand it was again found that by oxidation (50 mm. of O₂ at 320° C for an hour) and subsequent reduction the rates of both diffusion and conversion were increased (cf. Fig. 6 curves III for diffusion and IV for conversion on the inside). In this case, however, the rate of conversion was only twice as fast as the rate of diffusion, and it was not possible even after a second activation by oxidation and reduction) to obtain on the inner side

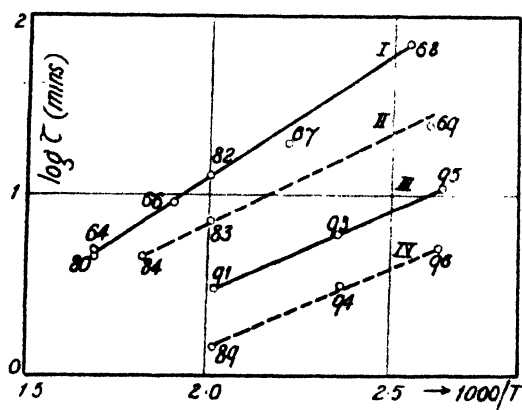


FIG. 6.—Diffusion and conversion on the tube some days later than Fig. 5.

I = rate of diffusion, energy of activation 6 Kcals.

II = rate of conversion on inner side, energy of activation 4.5 Kcals.

Tube oxidised and reduced:

III = rate of diffusion, energy of activation, 4.2 Kcals.

IV = rate of conversion on inner side, energy of activation 4.1 Kcals.

of the tube such a high activity as is shown on the outer side, owing probably to the presence of some non-volatile impurity in the tube.

The Comparison of the Rates of Diffusion for H₂ and D₂.

In a previous paper by A. and L. Farkas⁴ the relative rates for the diffusion of hydrogen and deuterium were investigated by allowing a mixture of hydrogen and deuterium to diffuse through a palladium tube and determining the composition of the diffusing gas. The ratio $(H/D)_{diff.}/(H/D)_{orig.}$ characterising the relative diffusion rates of hydrogen and deuterium, where $(H/D)_{diff.}$ and $(H/D)_{orig.}$ denote the ratio of hydrogen and deuterium in the diffused gas and in the original gas respectively) was higher than unity and varied with temperature. The temperature variation was explained by assuming that the energy

⁴ A. Farkas and L. Farkas, *Proc. Roy. Soc.*, 1934, 144, 467.

of activation for the diffusion of hydrogen and deuterium differs by some 800 cals.

Jost and Wiedemann⁵ who compared directly the diffusion rates of hydrogen and deuterium into a palladium sphere could not substantiate this dependence of the relative rates on temperature, but showed that the ratio for the diffusion of hydrogen and deuterium is very nearly $\sqrt{2}$, i.e. the value to be expected from their different masses. These authors also pointed out the necessity, according to Wagner, of ascertaining whether the diffusion rate is governed by the boundary process or not. They assumed that by palladising their sphere they made the surface sufficiently active to eliminate the surface reaction. No direct comparison of their experiments with those of A. and L. Farkas was possible since the latter undoubtedly involved a surface reaction having a very much higher activation energy (17 Kcals.) than in Jost and Wiedemann's experiments (5 Kcals.). On the other hand the direct comparison of the diffusion rates of hydrogen and deuterium through a palladium tube by Melville and Rideal² yielded results comparable with those of A. and L. Farkas.

It seemed desirable, therefore, to compare again the relative diffusion rates for the hydrogen isotopes, particularly since by using the very permeable palladium sample the investigations could be extended over a wider range of temperature and, moreover, by comparing not only the diffusion rates but also the conversion rates for the hydrogen isotopes it should be possible to decide whether the process on the boundary or that in the bulk of the palladium was responsible for the different diffusion rates.

In the diffusion experiments *ortho*-deuterium was used (containing about 90 per cent D) and the rate of its conversion determined in the usual way. The results of the experiments comparing the diffusion rates and conversion rates for the hydrogen isotopes is summarised in Tables II. and III.

From these experiments we conclude that:

1. The ratio of the diffusion rates of hydrogen and deuterium through palladium is only slightly dependent on temperature and varies from 1.24 to 1.84 in the temperature region of 186 to 20° C.

2. The ratio of the conversion of *para*hydrogen and of *ortho*deutrium is about the same.

3. The energies of activation for the diffusion of hydrogen and deuterium determined from the dependence of the diffusion rate on temperature are equal within the limits of experimental error, being 5.4 and 5.3 Kcals. respectively.

TABLE II.—COMPARISON OF ENERGIES OF ACTIVATION FOR DIFFUSION. DISC (ORIGINAL ACTIVITY).

No.	°C.	Gas.	Half-life of Diffusion.	Energy of Activation in Kcals.
2	312	D ₂	3	5.3
3	240	D ₂	6	
4	186	D ₂	11	
5	186	H ₂	9	5.4
6	119	H ₂	28	
7	70	H ₂	68	

Discussion.

A complete theoretical treatment of the diffusion of hydrogen through palladium is complicated for two main reasons: (1) The actual process

⁵ W. Jost and A. Wiedemann. *Z. physik. Chem., B*, 1935, **29**, 247.

TABLE III.—COMPARISON OF DIFFUSION AND CONVERSION RATES.

No.	Catalyst and Treatment.	°C.	Gas.	Half-Life of	
				Conversion.	Diffusion.
				Minutes. Ratio.	Minutes. Ratio.
4	Disc original	186	D ₂	—	11 } 1.24
5	" "	186	H ₂	—	9 }
14-15	Disc original (conversion on the upper side)	131	H ₂	6.5 } 1.02	25 } 1.36
16-17	Disc original	131	D ₂	12.5 }	34 }
21	Disc original on lower side	-30	{ H ₂ D ₂	6.5 } 1.54	—
25	Disc activated	20	H ₂	—	31 } 1.84
29	" "	20	D ₂	—	57 }
95	Tube activated	106	H ₂	—	10.7 } 1.40
97	" "	106	D ₂	—	15 }

of diffusion consists of several different individual processes. (2) The two sides of a palladium sample are in general not identical, so far as catalytic activity is concerned, and processes occurring on different sides involve different velocity constants.

We shall consider now, however, only simplified cases, in order to find out the characteristics of the diffusion process, such as dependence on pressure and on temperature. Thus it will be assumed that there are only three different processes on the boundaries and in the bulk of the metal:

(a) Sorption of hydrogen on the surface of the metal involving a dissociation of molecular hydrogen into atoms;

(b) Diffusion of the hydrogen atoms from one boundary to the other through the bulk of the metal;

(c) Desorption of hydrogen from the boundary involving a recombination of molecules from the atoms.

The term "sorption" is used here to designate the boundary reaction which has a hydrogen molecule in the gaseous phase as initial state and dissociated hydrogen on or beneath the surface of the metal as final state, the term "desorption" being used for the reverse reaction. Thus no discrimination is made between two or more consecutive processes occurring on the boundary, such as "activated adsorption" in the sense of H. S. Taylor⁶ (transfer of hydrogen molecules from the gas phase to the surface of the metal, involving some loosening of the molecular bond) followed by "penetration" used by Melville and Rideal⁴ (a boundary process involving transfer of hydrogen atoms from the surface into the first layer inside the metal). Melville and Rideal assume from recent experiments of Roberts⁷ that the actual process of adsorption, even if involving a breakage of molecular bonds, has a negligible energy of activation and they regard penetration as the process characteristic for the boundary. If this assumption can be made generally their term "penetration" has the same meaning as the term "sorption" used in this paper.

⁶ H. S. Taylor, *J. Am. Chem. Soc.*, 1930, **52**, 5298; 1931, **53**, 578.

⁷ J. K. Roberts, *Proc. Roy. Soc.*, 1935, **152**, 445.

As a further simplification a possible difference in the activity and effective area of the two metal/gas boundaries will be neglected. Thus, assigning to the above-mentioned processes the velocity constants k_a , k_b , and k_c , denoting by x and y the concentration of the atoms on the boundaries and by C the concentration of hydrogen in the gas phase we find

$$\begin{aligned} k_a C &= k_c x^2 + k_b(x - y) \\ k_b(x - y) &= k_c y^2 \end{aligned}$$

where $k_c x^2$ is the observed rate of the *para*-hydrogen conversion and the expression $k_b(x - y)$ arises since the net diffusion is equal to difference of the forward and backward diffusion. This is the quantity actually observed in diffusion experiments.

In examining the effect of pressure we have to distinguish two limiting cases:

(1) The diffusion is very slow compared with the rate of the adsorption and desorption, i.e. $y \ll x$ therefore

$$x = \sqrt{\frac{k_a C}{k_c}}$$

or the net diffusion

$$k_b x = k_b \sqrt{\frac{k_a C}{k_c}}$$

is proportional to the square root of the concentration or pressure.

(2) The diffusion is very rapid, i.e. $y \approx x$ then

$$k_a C = 2k_c x^2$$

or the net diffusion

$$k_c x^2 = \frac{k_a C}{2}$$

is proportional to the concentration or pressure.

It was found experimentally that the diffusion is proportional to the square root of the pressure, but this result must be regarded as merely accidental since in most experiments none of the conditions is strictly fulfilled under which this simple relationship is to be expected: both boundaries generally have distinctly different activities and the net diffusion is of the same order of magnitude as the adsorption or the *para*-hydrogen conversion. Only in the experiments with the activated palladium disc (Nos. 25 to 28, Fig. 4) are the reactions on the boundaries sufficiently rapid to explain the square root law.

The next question is the relation between the energies of activation of the processes observed experimentally, i.e. conversion of *para*-hydrogen and net diffusion, and those of the individual processes of sorption, diffusion of atoms and desorption.

Even in the general case, when the activity is different on different sides of the palladium sample, the sum of the rate of conversion plus net diffusion is the rate of adsorption. Thus we can obtain the energy of activation (A_a) for this process from the dependence of the mentioned sum on temperature.

Since the conversion is always larger than the diffusion and furthermore the dependence of the net diffusion on temperature is nearly the same as that of the conversion we find as energy of activation for the sorption process the same value as the energy of activation for the conversion.

The difference between the energies of activation for desorption (A_d) and sorption is the heat of adsorption. This quantity is probably of the order of 2 Kcals., *i.e.* near the value of the heat of absorption (*cf.* Melville and Rideal² and Sieverts and Zapf.⁸).

The energy of activation for the actual diffusion of the atoms through the bulk of the metal (A_b) can be obtained as follows from the experiments with the activated disc (Nos. 25 to 28). The diffusion being very much slower than the conversion, we obtain for the net diffusion

$$k_b x = k_b \sqrt{k_a C / k_c}$$

or since

$$k_a \propto \exp(-A_a/RT), k_b \propto \exp(-A_b/RT) \text{ and } k_c \propto \exp(-A_c/RT)$$

$$k_b x \propto \exp[(-A_b + Q/2)/RT]$$

Consequently the true energy of activation for the atomic diffusion is higher by half the heat of sorption than the apparent energy of activation for the diffusion observed on the activated disc.

With $Q = 2$ Kcals. we obtain an energy diagram as shown on Fig. 7 for the palladium disc in its original state (*i.e.*, before the activation). Since the hydrogen diffuses within the metal in atomic form, the figure refers to $\frac{1}{2}H_2$ and therefore only half of the energy of activation for the sorption A_a' and A_a'' appears on the boundaries; *i.e.*, 2.9 and 1.15, instead of 5.8 and 2.3 Kcals. (*cf.* page 1670).

This energy diagram is modified after the activation of the palladium disc; the energy barrier on the left-hand side connected with the sorption and dissociation of hydrogen is considerably decreased (shown in Fig. 7 by the dotted line) and the rate of diffusion is determined by the highest barrier, *viz.* that connected with the transfer of hydrogen atoms in the bulk of the metal.

It seems justifiable to assume that inside the palladium the energy barrier is the same before and after activation, since by the superficial oxidation and reduction the surface properties alone and not the interior of the metal have been altered.

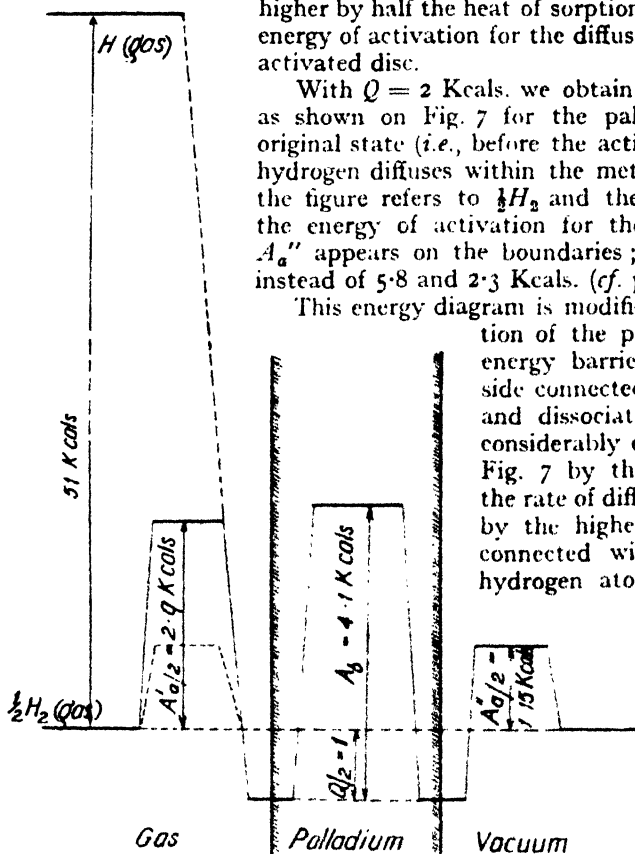


FIG. 7.—Energy diagram for the diffusion of hydrogen through the palladium disc (original state):

- A_a' = energy of activation for sorption on the upper side.
- A_a'' = energy of activation for sorption on the lower side.
- A_b = energy of activation for diffusion.
- Q = heat of sorption.

⁸ A. Sieverts and G. Zapf, *Z. physik. Chem.*, A, 1935, 174, 359.

With the palladium tube we have essentially the same state of affairs. If we assume the same conditions inside the bulk of the tube as has been found for the disc, the energy barriers for the tube can be represented as those in Fig. 7 with $A_a' = 9.6$ and $A_a'' = 5.4$ Kcals. One difference, however, must be mentioned. It is not the higher barrier of 9.6 Kcals. which determines the rate of diffusion of hydrogen but the lower one of 5.4 Kcals., since, as already mentioned, the strong hindrance of the boundary reaction caused by the high energy of activation appears to be over-compensated by a very large effective area (or some other factor independent of temperature).

We consider finally the different rates of diffusion for H_2 and D_2 . This difference is caused either by different molecular (or rather atomic) velocities on and inside the metal, due to the difference in the masses, or by a difference in the energies of activation.

In the former case the dependence of the ratio on temperature should be less than that observed. In the latter, a difference in the energies of activation for the diffusion of H_2 and D_2 of 200-300 calories would account for the absolute value of the ratio, though its dependence on temperature would suggest a difference of 660 cal. Assuming this value the ratio of the diffusion rates of the two hydrogens (v_H/v_D) is formally represented by the expression (cf. Table IV.).

$$v_H/v_D = 0.6 e^{-660/RT}$$

though it is not quite clear why the factor 0.6 occurs.

It is difficult to decide which explanation is correct, since, owing to the relatively small dependence of the rates on temperature and the possible experimental error, the variation actually observed may only be accidental.

Moreover, from the formula opposite a higher ratio is to be expected for the conversion velocities of *parahydrogen* and *orthodeuterium* at -30°C. than is observed (see Table III).

It is therefore not easy to determine with certainty the cause of a difference in reaction velocity from a mere comparison of the velocities of heterogeneous reactions involving the hydrogen isotopes and their compounds.

TABLE IV.

Temperature $^\circ \text{C.}$	Ratio	
	Observed.	Calculated.
186	1.24	1.25
131	1.36	1.37
106	1.40	1.45
20	1.84	1.87

Conclusions.

From the present results we can understand why hydrogen diffuses so rapidly through metals in electrolysis; the hydrogen is supplied to the metal in atomic form and thus the hindrance due to the energy of activation for dissociation is eliminated (see Fig. 7). Furthermore it is also evident that the actual heights of the barrier on either side of the metal do not determine the diffusion rate, provided that the barrier on the entrance side is not lower than that on the outlet side. Owing to the supply of atomic hydrogen the bulk of the metal becomes saturated and then the hydrogen "overflows" over the edge of the outlet barrier.

This picture serves to explain some observations of Kobosew and

Monblanowa⁹ on the effects of electrolytes and poisons on the electrodiffusion of hydrogen through a palladium membrane. Electrolytes, (specially K^+ ions) and poisons (such as pyridine or sodium arsenate) accelerate the rate of diffusion if applied on the entrance side of the membrane but have an inhibiting effect if applied on the other side. A poisoning of the entrance side prevents the atoms from recombining and thus forces them to leave the metal through diffusion, on the other hand, a blocking up of the exit side must necessarily lead to a backward diffusion, so that more and more hydrogen will leave the membrane on the same side as entered.

Melville and Rideal⁸ obtained the apparent energies of activation shown in Table V. for the diffusion of hydrogen through a palladium disc and tube with and without an electro-deposited surface layer of copper and nickel.

TABLE V—ENERGY OF ACTIVATION IN Kcals.

	Uncovered.	0.0034 cm. Cu.	0.00038 cm. Ni.
Tube .	17.8	13.7	14.3
Disc .	5.0	11.4	—

The considerable effect of the coating is to be attributed entirely to a change in the surface conditions of the palladium, since naturally by

the electro-deposition of the Cu or Ni-layer the inside of the palladium has not been changed at all.

Finally a group of experiments by Coehn and co-workers¹⁰ carried out on wires, one portion of which was saturated electrolytically with hydrogen, allows a direct determination of the energy of activation for the actual diffusion inside the palladium. The spreading of hydrogen inside the wire was followed up by measuring the change in the electric resistance or potential of certain portions of the wire. From the dependence of the coefficient of diffusion on temperature one finds an energy activation of 4.9 to 6.7 Kcals. These figures are actually characteristic of the transfer of hydrogen inside the metal, no processes on the boundaries being involved, and are in satisfactory agreement with the value of 4 Kcals. obtained in this paper (see Fig. 7).

Summary.

The rate of diffusion of hydrogen through a palladium disc and tube has been compared with the rate of the conversion of *para*-hydrogen at temperatures of 20 to 320° C. and about at 20 mm. Hg.

Applying this method one can decide whether and to what extent the reactions occurring on the metal/gas boundaries determine the rate of diffusion.

Two characteristic cases were isolated: The *para*-hydrogen conversion is (1) about 3-4 times quicker than the diffusion and its dependence on temperature is approximately the same as that of the diffusion; (2) very much faster than the diffusion and has a smaller temperature coefficient than the diffusion.

In the former case the boundary reaction is the rate-determining step for the diffusion and consists in a dissociation of the hydrogen molecule, being also responsible for the conversion of *para*-hydrogen; in the latter,

⁹ N. I. Kobosew and W. W. Monblanowa, *Acta Phys.-Chem. U.S.S.R.*, 1934, 1, 611.

¹⁰ A. Coehn and co-workers, *Z. Physik*, 1930, 62, 1; 1931, 71, 179; 1933, 83, 291.

the rate of diffusion is governed by the actual transfer of the hydrogen atoms in the bulk of the palladium.

Though the rate of diffusion does not depend on the direction of diffusion, the rate of the *para*-hydrogen conversion may be different on different sides of the disc or tube, indicating the two sides may have entirely different catalytic activities.

From the apparent energies of activation for the *para*-hydrogen conversion on both sides of a palladium sample and the energy of activation for the diffusion (calculated from the dependence of the corresponding rates on temperature) the energy levels for the primary processes occurring in the diffusion can be determined. Such processes are (1) The sorption of molecular hydrogen involving dissociation; (2) transfer of atomic hydrogen through the bulk of the palladium; (3) desorption of molecular hydrogen. For example the following energies of activation were found for a palladium disc with sides of different activity for sorption (entrance side) 5.8 Kcals.; for transfer 4.1 Kcals.; for desorption (exit side) 3.3 Kcals. Rate determining step = Sorption.

A comparison of the rates of diffusion for hydrogen and deuterium shows that the former diffuses slightly more quickly, but the cause of this behaviour cannot be given with certainty.

Some recent experiments on the diffusion of hydrogen through palladium are discussed in the light of these results.

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TEMPERATURE COEFFICIENTS OF ELECTRICAL CONDUCTIVITY OF ELECTROLYTES IN METHYL AND ETHYL ALCOHOLS.

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The present work is concerned with the measurement of the electrical conductivities of solutions of certain salts, bases and of hydrogen chloride in methyl and ethyl alcohols at 25°, 15° and 4° C., and the conclusions which may be drawn from the results. From the conductivity curve of an electrolytic solution it is possible to obtain the limiting conductivity at infinite dilution (Λ_0) and the degree of deviation of the curve from the theoretical Debye-Hückel-Onsager straight line. Fuoss and Krauss¹ have given a method by which, assuming the deviation to be due to incomplete dissociation of the electrolyte, Λ_0 and a consistent "true" dissociation constant (K) may be calculated. By obtaining values for these quantities over a range of temperature the variation of $\Lambda_0\eta$ may be measured (η being the viscosity of the solution), also the mean heat of dissociation of the electrolyte: the former may be used to test Walden's rule (constancy of $\Lambda_0\eta$) and to

¹ *J. Amer. Chem. Soc.*, 1933, **55**, 476.

throw light on the precise mechanism of transport of ions ; the latter may be compared with the experimental integral heats of dilution of electrolytes.

The investigation has been carried out with these objects in view : the intention has been rather to explore the field than to work it in great detail.

Previous Work.

Not many measurements of conductivity curves at different temperatures have been made : the earlier work was not carried to high enough dilutions for accurate extrapolation to be possible. The following comprise the more recent investigations :—

Authors.	Solvent.	Electrolytes.	Temperatures.
Walden and Ulich ²	Water	Uni-univalent salts.	0°, 18°, 100°
Ekwall ³	„	Substituted ammonium salts	0°, 25°, 90°
Johnston ⁴	„	Higher valency type salts	
Walden and Ulich ⁴	Methyl and ethyl alcohols	} Salts	0°, 25°, 56°
Walden, Ulich and Laun ⁴			
Walden, Ulich and Busch ⁷	Acetone	Salts	0°, 25°, 50°
Martin ⁸	Benzonitrile	Salts	0°-70°
Philip and Oakley ⁹	Nitromethane	Potassium Iodide	0°-85°

In all these investigations the interest is centred on the constancy or otherwise of $\Lambda_{0\eta}$ and $l_{0\eta}$. Their results may be summarised : in the non-hydroxylic solvents $\Lambda_{0\eta}$ and $l_{0\eta}$ are constant or increase slightly with increasing temperature, but in hydroxylic solvents much larger variations occur usually in the opposite sense, *i.e.* they decrease with rise of temperature. The salts having large and comparatively unsolvated ions obey Walden's rule most closely.

Experimental.

Measurements of electrical conductivity were made by the method of Murray-Rust and Hartley.¹⁰ The constants of the cells used were determined from time to time using solutions of potassium chloride in methyl alcohol at 25° C, and were based on Fraser and Hartley's values.¹¹ The variation of cell constant with temperature is negligible.

The temperature of the water thermostat was controlled by heating lamps actuated by a toluene regulator through a relay. Cold tap water was circulated through a copper cooling coil at 15° C and ice water at 4° C at a rate sufficient to give equal periods of heating and cooling. The temperatures were checked from time to time against an NPL standard and were maintained constant within 0.01° C.

² *Z. physikal. chem.*, 1923, 106, 49 ; 107, 219.

³ *Ibid.*, 1932, 161, 211.

⁴ *J. Amer. Chem. Soc.*, 1909, 1012.

⁵ *Z. physikal. chem.*, 1924, 114, 297.

⁶ *Ibid.*, 114, 275.

⁷ *Ibid.*, 1926, 123, 429.

⁸ *J.C.S.*, 1928, 3270 ; 1930, 530.

⁹ *Ibid.*, 1924, 125, 1189.

¹⁰ *Proc. Roy. Soc., A*, 1929, 126, 84.

¹¹ *Ibid.*, 1925, 109, 351.

Materials.

Methyl alcohol was prepared by the method of Hartley and Raikes,¹² ethyl alcohol by that of Copley, Murray-Rust and Hartley.¹³

Potassium chloride and iodide, lithium iodide, silver nitrate, tetraethyl ammonium perchlorate and picrate were taken from stocks of these salts purified for conductivity purposes by previous workers in this laboratory. Potassium chloride and iodide, tetraethyl ammonium picrate and perchlorate were dried to constant weight in an electric oven at 250°, 220°, 120° and 110° C. respectively; silver nitrate was dried in a small vacuum oven over phosphorus pentoxide at 80° C. Lithium iodide had been twice recrystallised from water; it was dried in the vacuum oven at 50° C. for a fortnight and the temperature then raised to 70° C. for a week without the salt becoming discoloured; the composition reached corresponded closely by analysis and in the conductivity results to $\text{LiI} \cdot \frac{1}{2} \text{H}_2\text{O}$. (The amount of water introduced into solution is negligible since the driest methyl alcohol obtainable contains about 0.03 per cent. of water.) B.D.H. tetraethyl ammonium bromide contained impurities after recrystallisation from ethyl alcohol; heating in a vacuum oven at 70° C. caused part of the salt to sublime, and after several weeks both analysis and the conductivity gave results agreeing with the formula NEt_4Br .

Solutions of hydrochloric acid were prepared by the method of Murray-Rust and Hartley¹⁰ and used on the day of their preparation; their estimation followed the method described by Jones and Hughes.¹⁴

Solutions of potassium methoxide, ethoxide, methyl carbonate and ethyl carbonate were prepared by Jones and Hughes; the measurements on them were made in collaboration with those authors.

Results.

(1) The results of the conductivity measurements are given in Tables I., II. and III. (Column 1: Temperature and specific conductivity of the solvent (k). Column 2: concentration in gm. equivs./litre. Column 3: equivalent conductivity. Column 4: Λ_{corr} , the corrected conductivity of bases and of hydrogen chloride in ethyl alcohol.) At the foot of each run is given x , the slope of the linear part of the curve and α , the Debye-Hückel-Onsager slope. In calculating α , the values for the dielectric

TABLE I.—METHYL ALCOHOL.

k .	$C \times 10^4$.	Λ_c .	k .	$C \times 10^4$.	Λ_c .		
Potassium Chloride at 15° C.			Potassium Chloride at 4° C.				
Series A	0.055	1.2793	88.32	Series A	0.044	0.88349	74.97
		2.4836	87.37			1.8410	74.27
		4.3439	86.25			3.7006	73.23
		6.0567	85.43			6.0209	72.33
		8.7938	84.35			8.5313	71.48
		11.6114	83.39			11.6185	70.65
Series B	0.006	1.2437	88.42	Series B	0.044	1.1555	74.82
		2.3300	87.51			2.0119	74.16
		3.9796	86.52			3.8008	73.18
		6.0224	85.46			6.3184	72.18
		8.7139	84.38			9.1354	71.31
		11.7553	83.36			12.185	70.50
$x = 218 \quad \alpha = 207.2$			$x = 177 \quad \alpha = 170.2$				

¹² J.C.S., 1925, 127, 524.

¹³ *Ibid.*, 1930, 2492.

¹⁴ *Ibid.*, 1934, 1197.

TABLE I.—*Continued.*

	λ .	$C \times 10^4$.	A_e .		λ .	$C \times 10^4$.	A_e .
Silver Nitrate.							
25° C.	0.043	1.3906	106.98	15° C.	0.037	1.0283	112.52
		2.5101	105.54			2.6473	110.30
		4.7383	102.94			4.8975	108.17
		8.0227	99.95			6.9648	106.53
		11.2667	97.56			9.3542	104.69
		15.3419	94.91			13.5758	102.29
	$x = 460$	$\alpha = 251.3$			$x = 400$	$\alpha = 229.1$	
15° C.	0.036	1.3666	93.21	4° C.	0.032	1.0713	96.48
		2.6259	91.81			2.6208	94.67
		4.6865	89.74			4.9707	92.79
		8.1609	87.23			7.0720	91.41
		11.5189	85.16			9.5058	89.91
		15.5958	83.14			13.6524	87.74
	$x = 372$	$\alpha = 213.2$			$x = 350$	$\alpha = 190.1$	
4° C.	0.039	1.3970	79.11	Tetraethyl Ammonium Bromide.			
		2.5392	78.12	25° C.	0.036	1.0580	114.77
		4.4954	76.59			2.2720	113.64
		7.9350	74.50			4.5297	111.73
		11.2391	72.82			6.9871	110.14
		15.2235	71.13			10.246	108.09
	$x = 310$	$\alpha = 175.9$				13.482	106.78
Potassium Methyl Carbonate.					$x = 322$	$\alpha = 255.4$	
25° C.	0.054	3.037	93.76	4° C.	0.029	1.4386	85.45
		5.532	92.05			2.6503	84.67
		8.644	90.36			4.7370	83.49
		12.217	88.57			7.2990	82.25
		16.522	87.05			10.732	80.79
	$x = 291$	$\alpha = 239$				14.202	79.76
15° C.	0.037	2.462	81.98		$x = 240$	$\alpha = 179.4$	
		4.941	80.41	Tetra Ethyl Ammonium Picrate.			
		7.508	79.15	25° C.	0.030	0.78887	105.83
		10.756	77.88			1.5111	104.82
		14.450	76.57			2.8029	103.44
	$x = 243$	$\alpha = 203$				4.6566	102.02
4° C.	0.033	2.626	69.18			6.7349	100.66
		5.518	67.80			9.0101	99.39
		7.466	67.03		$x = 303$	$\alpha = 247.5$	
		10.863	66.02	15° C.	0.034	0.76799	92.24
		14.235	65.11			1.5143	91.33
	$x = 188$	$\alpha = 167$				3.1525	89.94
Tetra Ethyl Ammonium Perchlorate.						4.8630	88.83
25° C.	0.037	0.96507	128.42			6.8029	87.79
		2.2259	126.39			9.2944	86.71
		4.1060	124.10		$x = 255$	$\alpha = 210.2$	
		6.0316	122.16	4° C.	0.027	0.78186	78.92
		8.4944	119.91			1.6270	77.89
		12.5898	117.08			3.0112	76.92
	$x = 460$	$\alpha = 268.6$				4.8685	75.90
						7.0292	74.98
						9.6469	73.98
					$x = 215$	$\alpha = 173.8$	

TABLE I.—Continued.

	<i>h</i> .	$C \times 10^4$.	A_g .
Hydrogen Chloride.			
25° C.	0.038	2.001	187.71
		4.372	186.30
		7.807	183.38
		10.928	181.38
		14.869	179.41
$\alpha = 375$		$\alpha = 319$	
15° C.	0.033	2.085	168.11
		4.597	166.41
		7.927	164.29
		11.426	162.31
		15.368	160.65
$\alpha = 330$		$\alpha = 276.5$	
4° C.	0.035	2.437	145.77
		4.919	144.20
		8.118	143.01
		11.651	141.16
		15.693	139.70
$\alpha = 290$		$\alpha = 233$	

TABLE IA. METHYL ALCOHOL.

λ .	$C \times 10^4$.	A_g .	A_g (corr.).
Potassium Methoxide.			
25° C. 0.033	3.428	99.86	102.00
	5.851	99.39	100.71
	9.486	98.09	98.91
	13.84	96.66	97.27
	17.56	95.68	96.17
		$\alpha = 250$	$\alpha = 245.5$
15° C. 0.036	1.7201	86.83	88.60
	3.661	86.56	87.43
	5.831	85.88	86.45
	9.529	84.73	85.09
	13.499	83.55	83.81
	17.792	82.64	82.85
		$\alpha = 196$	$\alpha = 208.5$
4° C. 0.039	1.625	71.91	74.10
	3.456	72.18	73.21
	5.709	71.70	72.34
	8.674	71.06	71.50
	12.392	70.28	70.60
	17.108	69.37	69.60
		$\alpha = 157$	$\alpha = 170$

TABLE II.—ETHYL ALCOHOL.

	<i>h</i> .	$C \times 10^4$.	A_g .
Potassium Iodide.			
25° C.	0.0085	0.65246	47.99
		1.5363	47.51
		2.5849	46.79
		4.4740	45.87
		6.1126	45.02
		8.2691	44.18
		11.8163	43.05
$\alpha = 200$		$\alpha = 152.5$	
15° C.	0.0072	0.9818	39.64
		2.4599	38.85
		4.2764	38.06
		6.1868	37.37
		8.4013	36.73
		12.2581	35.78
		$\alpha = 159$	
4° C.	0.0072	0.9873	31.79
		2.3186	31.25
		4.4984	30.33
		6.3003	30.08
		8.6010	29.56
		12.6080	28.85
		$\alpha = 117$	

	<i>h</i> .	$C \times 10^4$.	A_g .
Lithium Iodide.			
25° C.	0.022	1.1351	42.24
		2.4221	41.52
		4.3912	40.65
		7.4247	39.65
		10.5459	38.88
		13.9890	38.15
		$x = 153$	$\alpha = 144.9$
15° C.	0.015	1.0970	34.85
		2.5061	34.22
		4.3794	33.56
		[6.7438	32.69]
		9.9376	32.26
		13.4454	31.68
		$x = 122$	$\alpha = 116.7$
4° C.	0.007	1.1264	27.92
		2.6993	27.40
		4.7472	26.87
		7.0501	26.41
		9.7752	25.97
		13.5582	25.48
		$x = 94$	$\alpha = 92.4$

TABLE II.—Continued.

	λ .	$C \times 10^4$.	Λ_c .		λ .	$C \times 10^4$.	Λ_c .
Tetra Ethyl Ammonium Perchlorate.				Tetra Ethyl Ammonium Picrate.			
25° C.	0.0133	0.38429	59.83	25° C.	0.0097	0.86945	52.44
		1.2280	57.98			1.9036	51.26
		2.2459	56.31			2.8853	50.38
		3.1758	55.02			4.1667	49.43
		4.3176	53.70			5.5474	48.57
		6.3346	51.75			7.9705	47.27
	$x = 450$	$\alpha = 167.0$			$x = 278$	$\alpha = 158.7$	
15° C.	0.0112	0.69392	49.10	15° C.	0.0089	0.84435	43.61
		1.3350	48.03			1.7800	42.74
		2.3257	46.77			2.9005	41.95
		3.3210	45.67			4.1393	41.22
		4.4352	44.63			5.5610	40.48
		6.4001	43.07			7.9171	39.48
	$x = 367$	$\alpha = 135.0$			$x = 223$	$\alpha = 127.8$	
4° C.	0.0078	0.76900	39.62	4° C.	0.0075	0.99575	35.09
		1.8028	38.40			1.8846	34.40
		2.4837	37.75			2.9301	33.88
		3.7545	36.68			4.0519	33.39
		4.8865	35.84			5.6371	32.74
		7.0103	34.55			8.1461	31.92
	$x = 303$	$\alpha = 107.1$			$x = 176$	$\alpha = 101.2$	

TABLE III.—ETHYL ALCOHOL.

	λ .	$C \times 10^4$.	Λ_c .	Λ_c (corr.).		λ .	$C \times 10^4$.	Λ_c .	Λ_c (corr.).
Hydrogen Chloride.					Potassium Ethoxide.				
25° C.	0.0095	2.439	77.14	77.17	25° C.	0.015	2.426	41.62	43.30
		4.732	75.26	75.28			3.915	41.37	42.56
		7.635	73.15	73.16			5.841	40.79	41.69
		10.790	71.31	71.32			9.025	39.82	40.47
		14.610	69.47	69.47			12.124	38.97	39.50
	$x = 354$	$\alpha = 195.3$					16.616	37.85	38.29
						$x = 204$	$\alpha = 148.5$		
15° C.	0.0089	2.251	63.95	63.98	15° C.	0.014	1.838	34.30	35.80
		4.697	62.47	62.48			3.797	34.06	34.93
		7.485	61.01	61.02			5.890	33.52	34.15
		10.815	59.52	59.53			8.619	32.86	33.35
		14.551	58.17	58.17			11.755	32.20	32.59
	$x = 264$	$\alpha = 156.9$					16.734	31.32	31.62
						$x = 155$	$\alpha = 119.0$		
4° C.	0.0072	2.439	50.91	50.94	4° C.	0.0075	1.851	27.52	28.20
		4.763	49.90	49.91			3.460	27.22	27.65
		7.863	48.77	48.78			5.622	26.78	27.09
		11.235	47.77	47.77			8.677	26.22	26.46
		15.246	46.84	46.84			11.245	25.79	25.99
	$x = 180$	$\alpha = 121.0$					16.279	25.19	25.34
						$x = 109$	$\alpha = 93.3$		

constants have been taken :—methyl alcohol,¹⁶ Lattey and Gatty ;¹⁸ ethyl alcohol, Lattey ;¹⁷ values of viscosities from the best values in Landolt-Börnstein and the International Critical Tables ; the values of Λ_0 were obtained by freehand extrapolation to the theoretical slope, and these seldom differed seriously from the final values obtained by exact extrapolation.

(2) Correction for the effect of impurities in the solvent was made : in the case of salts by subtracting the specific conductivity of the solvent ; in the case of bases and of hydrogen chloride in ethyl alcohol by the method

TABLE IV.

	25°.	15°.	4°.
Λ_0 in Methyl Alcohol.			
Potassium chloride	104.87 *	90.69	76.47
Hydrogen chloride	193.2	173.0	150.4
Tetra ethyl ammonium picrate	108.00	94.02	80.25
Potassium methyl carbonate	98.30	85.35	72.00
Tetra ethyl ammonium bromide	117.90	—	88.00
Tetra ethyl ammonium perchlorate	131.6	115.3	98.9
Silver nitrate	110.8	96.3	81.8
Potassium methoxide †	106.62	91.16	76.11

* Frazer and Hartley's data re-extrapolated.

† Linear extrapolation.

Λ_0 in Ethyl Alcohol.

Lithium iodide	43.80	36.08	28.92
Potassium iodide	49.65	41.03	32.83
Potassium ethoxide	46.15	37.60	29.54
Hydrogen chloride	81.70	67.30	53.25
Tetra ethyl ammonium picrate	54.15	45.00	36.30
Tetra ethyl ammonium perchlorate	61.40	51.00	41.15
Potassium ethyl carbonate	42.00	35.00	27.80

Dissociation Constants in Methyl Alcohol.

Potassium chloride	0.214	0.298	0.384
Hydrogen chloride	0.118	0.112	0.102
Tetra ethyl ammonium picrate	0.0581	—	0.0610
Potassium methyl carbonate	0.0576	0.0697	0.1050
Tetra ethyl ammonium bromide	0.0475	—	0.0441
Tetra ethyl ammonium perchlorate	0.0199	0.0202	0.0196
Silver nitrate	0.0153	0.0171	0.0187

Dissociation Constants in Ethyl Alcohol.

Lithium iodide	0.121	0.172	0.412
Potassium iodide	0.0212	0.0269	0.0392
Potassium ethoxide	0.0189	0.0240	0.0458
Hydrogen chloride	0.0112	0.0147	0.0232
Tetra ethyl ammonium picrate	0.00981	0.0103	0.01081
Tetra ethyl ammonium perchlorate	0.00366	0.00378	0.00394
Potassium ethyl carbonate	0.00286	0.00360	0.00446

¹⁶ 32.25, the value here used for the DEC of methyl alcohol at 25° C., is probably better than the value 30.3 used in previous papers from this laboratory.

¹⁷ *Phil. Mag.*, 1929, 7, 985.

¹⁸ *Private Communication.*

¹⁹ *J.C.S.*, 1934, 1197.

of Jones and Hughes; ¹⁸ no correction was applied to potassium methyl and ethyl carbonates or to hydrogen chloride in methyl alcohol for reasons given by those authors.

(3) Extrapolation of the curves was made by the method of Fuoss and Krauss,¹ and Λ_0 and K (Table IV.) obtained. Where K had comparatively large values an approximation to their method was sufficiently accurate: γ , the degree of dissociation was obtained from

$$1 - \gamma = \frac{\Lambda_0 - \Lambda - \alpha \sqrt{c}}{\Lambda_0 - \frac{3\alpha \sqrt{c}}{2}}$$

instead of by successive approximation in

$$\Lambda = \gamma (\Lambda_0 - \alpha \sqrt{\gamma c})$$

Potassium methoxide was found to have a slope less than the theoretical so that Λ_0 was obtained by the old method of graphical extrapolation.

(4) Values of $\Lambda_0\eta$ and of $\frac{\Delta\Lambda_0\eta}{\Lambda_0\eta\Delta T}$ are given in Table V. Table VI. gives approximate values of l_0 , $l_0\eta$ and of $\frac{\Delta l_0\eta}{l_0\eta\Delta T}$. These have been obtained on the assumption that $l_0\eta$ is constant with temperature for the picrate ion and by making reasonable assumptions of the temperature coefficients of $l_0\eta$ of other ions, where necessary.

TABLE V.—VALUES OF $\Lambda_0\eta$ AND MEAN TEMPERATURE COEFFICIENTS.

	$\Lambda_0\eta$.			$\frac{\Delta\Lambda_0\eta}{\Lambda_0\eta\Delta T} \times 10^4$.		
	25°.	15°.	4°.	25°-15°.	25°-4°.	15°-4°.
Methyl Alcohol.						
Potassium methyl carbonate	0.537	0.539 ₈	0.543	- 4.7		- 5.9
Potassium chloride . . .	0.572 ₈	0.573 ₈	0.577 ₈	- 1.8		- 6.3
Tetra ethyl ammonium picrate	0.590	0.594 ₈	0.605 ₈	- 7.6		-16.6
Silver nitrate	0.605	0.608 ₈	0.617 ₈	- 5.8		-13.4
Tetra ethyl ammonium perchlorate	0.719	0.728 ₈	0.746	-15.2		-21.6
Hydrogen chloride	1.055	1.091	1.135	-20.8		-38.6
Potassium methoxide . . .	0.582 ₈	0.576	0.574	+11.2		+ 3.2
Ethyl Alcohol.						
Potassium ethyl carbonate .	0.453 ₈		0.455		- 1.6	
Lithium iodide	0.473		0.472 ₈		+ 0.5	
Potassium iodide	0.536 ₈		0.536 ₈		0.0	
Tetra ethyl ammonium picrate	0.585		0.593 ₈		- 6.9	
Tetra ethyl ammonium perchlorate	0.663		0.673		- 7.1	
Hydrogen chloride	0.882 ₈		0.870		+ 6.8	
Potassium ethoxide	0.499		0.483		+15.5	

(5) Table VII. gives mean values of the heats of dissociation in two temperature ranges, derived from the dissociation constants by the integrated Van't Hoff isochore

$$Q = - 2.303 \frac{RT_1T_2}{T_1 - T_2} \left(\log \frac{K_1}{K_2} - \log \frac{d_1}{d_2} \right),$$

TABLE VI.—VALUES OF l_0 , OF l_{07} AND OF THE MEAN TEMPERATURE COEFFICIENTS OF l_{07} .

Ion.	25°.		4°.		$\frac{\Delta l_{07}}{l_{07} \Delta T} \times 10.4$
	l_0 .	l_{07} .	l_0 .	l_{07} .	25°-4°.
Methyl Alcohol.					
Methyl carbonate	44.7	0.244	32.65	0.246	- 3.9
Picrate	46.5	0.254	34.1	0.257	- 5.6
Silver	49.7	0.271 ₅	36.6	0.276 ₅	- 8.7
Chloride	51.27	0.280	37.12	0.280	0.0
Potassium	53.6	0.293	39.35	0.297	- 6.5
Bromide	56.4	0.308	41.85	0.315 ₅	- 11.4
Nitrate	60.5	0.330 ₅	45.2	0.341	- 13.1
Tetra ethyl ammonium . . .	61.5	0.336	46.15	0.348 ₅	- 17.4
Perchlorate	70.1	0.383	52.85	0.398 ₅	- 18.9
Hydrogen	141.8	0.775	113.2	0.855	- 46.8
Methoxide	53.02	0.289 ₅	36.76	0.277 ₅	+ 20.1

Ethyl Alcohol.

Lithium	15.00	0.162 ₁	9.62	0.155 ₉	+ 18.6
Potassium	20.85	0.225 ₅	13.53	0.218 ₅	+ 15.4
Ethyl carbonate	21.15	0.228 ₂	14.27	0.231 ₂	- 6.2
Chloride	24.30	0.262 ₅	16.01	0.259 ₅	+ 5.3
Picrate	26.30	0.284 ₅	17.55	0.284 ₅	0.0
Tetra ethyl ammonium . . .	27.85	0.301 ₅	18.75	0.303 ₅	- 3.6
Iodide	28.80	0.311 ₄	19.30	0.312 ₄	- 1.8
Perchlorate	33.55	0.362 ₅	22.40	0.363 ₅	- 1.2
Hydrogen	57.40	0.620 ₉	37.24	0.603 ₅	+ 12.8
Ethoxide	25.35	0.274 ₀	16.01	0.259 ₅	+ 25.8

TABLE VII.—MEAN HEATS OF DISSOCIATION.

	25°-15° Calories.	25°-4° Calories.	15°-4° Calories.
In Methyl Alcohol.			
Potassium chloride	+ 5.450	—	+ 3.650
Silver nitrate	+ 1.760	—	+ 1,200
Potassium methyl carbonate . . .	+ 3.060	—	+ 6,070
Hydrogen chloride	- 1,100	—	- 1,560
Tetra ethyl ammonium perchlorate .	+ 70	—	- 660
Tetra ethyl ammonium picrate . .	—	+ 180	—
Tetra ethyl ammonium bromide . .	—	- 760	—
In Ethyl Alcohol.			
Lithium iodide	+ 5,800	—	+ 12,900
Potassium iodide	+ 3,900	—	+ 5,450
Potassium ethyl carbonate	+ 3,700	—	+ 3,100
Potassium ethoxide	+ 3,900	—	+ 9,500
Hydrogen chloride	+ 4,500	—	+ 6,700
Tetra ethyl ammonium perchlorate .	+ 410	—	+ 450
Tetra ethyl ammonium picrate . .	+ 640	—	+ 550

d_1 , d_2 being the densities of the solution (assumed equal to those of the pure solvent), K_1 , K_2 the dissociation constants, at temperatures T_1 , T_2 . These values of Q must be regarded as only approximate: insufficient statistical evidence is available to establish their accuracy.

Discussion.

Variation of $\Lambda_0\eta$ and $l_0\eta$.

The present results give general confirmation to those of previous workers in showing negative temperature coefficients of $\Lambda_0\eta$ and $l_0\eta$ in hydroxylic solvents; the following also appear to be true.

(1) In a given solvent the values of the temperature coefficient are more negative the greater are Λ_0 and l_0 , this is illustrated graphically

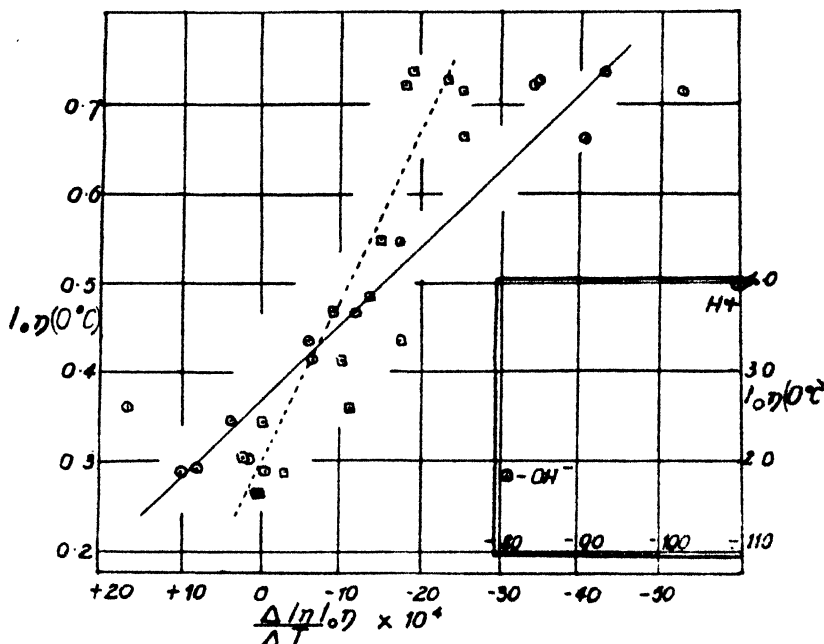


FIG. 1.—Temperature coefficients of $l_0\eta$ in water.

--- □ --- normal ions 18–100° C.

— ○ — normal ions 0–25° C.

Hydrogen and hydroxyl ions inset.

in the figure, in which values from the results of Walden and Ulich and of Ekwall in water are plotted. There is a roughly linear relationship between the temperature coefficient and Λ_0 or l_0 at a given temperature.

(2) The temperature coefficients have more negative values at lower than at higher temperatures.

(3) The temperature coefficients are on the whole increasingly negative in the order ethyl alcohol, methyl alcohol, water.

Since heats of solvation are in general positive, it does not seem possible to account for these negative temperature coefficients by an increase in ionic radius with temperature: moreover, the systematic differences between behaviours of salts in the two classes of solvents would be hard to explain on this basis, and it seems more likely that

the cause is to be found in the nature of the solvent rather than of the ions.

The experiments of Bridgman¹⁹ on the effect of pressure on the viscosity of liquids showed that in this property also the behaviour of hydroxylic solvents is peculiar. They are "abnormal" since increase of pressure produces a smaller increase of their viscosity than in the case of "normal" (non-hydroxylic) liquids: it was shown that this abnormality increases in the order ethyl alcohol, methyl alcohol, water and in the case of water is less at higher than at lower temperatures. It seems likely that these two phenomena may be connected and that a pressure-viscosity effect is responsible for the negative temperature coefficients: a similar explanation of negative "B coefficients" in the viscosity equation has been suggested by Cox and Wolfenden.²⁰

The mechanism for producing such an effect is known to exist in the electrostriction of polar solvent by ions which Zwicky²¹ and Webb²² have shown must lead to very high pressures in the immediate neighbourhood of the ions: this will lead to values of the viscosity of solvent in this region different (generally greater) from those in the bulk of the solvent. Whatever may be the actual effective values of these viscosities, Bridgman's results show that, since non-hydroxylic solvents approach the behaviour of the normal with rise of temperature, the change in these effective viscosities with temperature must be more positive in the case of hydroxylic solvents than in the case of normal solvents. The change of ionic mobility with temperature will therefore be more negative in the former than in the latter, which will account for the more negative temperature coefficients of $A_0\eta$ and of $l_0\eta$. It seems reasonable to regard the zero or positive temperature coefficients found in non-hydroxylic solvents as normal, and the negative values in hydroxylic solvents as due to abnormality of the solvents presumably due to their complexity of liquid structure. It is natural that ethyl alcohol, methyl alcohol and water should be in the same order with respect to the magnitudes both of abnormality of temperature coefficients and of pressure-viscosity properties; also, since the higher the temperature the more nearly is this behaviour normal, the temperature coefficients also are more near to normal at higher than at lower temperatures.

Since the electrostriction pressure falls off very rapidly with distance from the centre of the ion, the abnormality should be most marked for the smallest and least for the largest ions: if A_0 or l_0 may be taken as an index of ionic size, this is found to be so.

The work of Bridgman, Zwicky and Webb shows that the viscosity should increase rapidly to very large values at a distance of 1 to 2 Å from the ion centre. The solvent immediately surrounding a very small ion is thus so viscous that it can crudely be regarded as moving entirely with the ion: it is not therefore surprising that the smallest (most mobile) ions have much the same mobilities in any given solvent.

To summarise, this very crude and imperfect picture, taking only electrostriction into account and treating the solvent as a continuum, gives a qualitative explanation of a number of facts.

¹⁹ *Proc. Nat. Acad. Amer.*, 1925, 11, 603.

²⁰ *Proc. Roy. Soc., A*, 1934, 145, 475.

²¹ *Physikal. Z.*, 1926, 27, 271.

²² *J. Amer. Chem. Soc.*, 1926, 48, 2589.

Abnormal Mobilities.

The ions of hydrogen in water and the alcohols and the hydroxyl ion in water have been regarded as having abnormally high mobilities; two essentially similar theories²³ have been put forward to account for this, both predicting the possibility of abnormal mobility wherever the ion in question can be derived from the solvent. Two criteria of abnormal mobility exist:

(1) Abnormally low temperature coefficients of mobility, predicted by both theories: these are evident in the case of the hydrogen ion in water and methyl alcohol (but not in ethyl alcohol) and of the hydroxyl ion (but not of the methoxide and ethoxide ions).

(2) The effect of small additions of water to alcoholic solutions,²⁴ producing large decreases of conductivity: this shows abnormal mobility of hydrogen ions in methyl and ethyl alcohols, but not of methoxide or ethoxide ions.²⁵

It appears from the present results that in the case of salts the temperature coefficients of $A_{0\eta}$ and $l_{0\eta}$ are related to A_0 or l_0 ; in every proved example of abnormal mobility the points of the temperature coefficients against A_0 or l_0 , when plotted, lie well off any line which can be drawn through the points for salts to describe this relation. The same is true for methoxide and ethoxide and suggests that a part of the mobility of these ions also is abnormal.

Heats of Dissociation and Dissociation Constants.

The heats of dissociation of salts having metallic kations are large and positive, those of tetra ethyl ammonium salts small and, in the case

TABLE VIII.—NEAREST DISTANCES OF APPROACH.

	From K , Å.	From Stokes' Law, Å.
In Methyl Alcohol, 25° C.		
Silver nitrate	2.30	5.46
Tetra ethyl ammonium perchlorate	2.66	4.55
Tetra ethyl ammonium bromide	4.86	5.00
Potassium methyl carbonate	4.98	6.12
Tetra ethyl ammonium picrate	5.15	5.62
Potassium chloride	7.54	5.69
In Ethyl Alcohol, 25° C.		
Potassium ethyl carbonate	2.47	7.15
Tetra ethyl ammonium perchlorate	2.57	4.94
Tetra ethyl ammonium picrate	3.65	5.56
Potassium ethoxide	5.32	6.56
Potassium iodide	5.87	6.21
Lithium iodide	10.03	7.63

of the bromide, negative. These results are in qualitative agreement with those of Jackson, Smith, Gatty and Wolfenden,²⁶ who found that the differences between the observed and calculated integral heats of dilution in methyl alcohol, were large and positive for metallic salts, but small and negative for tetra ethyl ammonium bromide. These differences

may in part represent the heats of dissociation involved in diluting solutions of incompletely dissociated electrolytes.

²³ Hückel, *Z. Elektrochem.*, 1928, **34**, 546; Bernal and Fowler, *J. Chem. Physics*, 1933, **1**, 515.

²⁴ Hughes and Hartley, *Phil. Mag.*, 1933, **15**, 610.

²⁵ Jones and Hughes, *J.C.S.*, 1934, 1197.

²⁶ *J.C.S.*, 1934, 1376.

The apparently deciding rôle of kations in determining the heat of dissociation is probably connected with their power of solvation, since dissociation of a molecule or ion pair must lead to increased solvation and metallic ions are known to be generally more highly solvated than tetra ethyl ammonium.

The dissociation constants of the salts are roughly in inverse order of their conductivities in accordance with the ion pair theory. The sums of radii of the ions of these salts have been calculated from Λ_0 by Stokes' Law and from K using the method of Fuoss and Krauss.¹⁷ (Table VIII.). Reasons have been given for supposing the values by the former method to be unreliable: those obtained by the latter method are at best only approximate.

Summary.

(1) The electrical conductivities of solutions in methyl alcohol of potassium chloride, silver nitrate, potassium methyl carbonate, tetra ethyl ammonium perchlorate, tetra ethyl ammonium picrate, tetra ethyl ammonium bromide, potassium methoxide and hydrogen chloride: in ethyl alcohol of potassium iodide, lithium iodide, potassium ethyl carbonate, tetra ethyl ammonium perchlorate, tetra ethyl ammonium picrate, potassium ethoxide and hydrogen chloride have been measured at 25°, 15° and 4° C.

(2) By the method of Fuoss and Krauss, the limiting conductivities and dissociation constants have been obtained.

(3) The negative temperature coefficients of $\Lambda_{0,7}$ and $l_{0,7}$ in hydroxylic solvents have been explained on the basis of the effect of electrostriction pressure on the local viscosity in the neighbourhood of ions.

(4) It is suggested that the methoxide and ethoxide ions exhibit abnormal mobility.

(5) Heats of dissociation have been calculated and compared with values of the integral heats of dilution of electrolytes in methyl alcohol.

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¹⁷ *J. Amer. Chem. Soc.*, 1933, **55**, 1010.

CHEMICAL REACTION IN ELECTRIC DISCHARGES. PART II. THE CHEMICAL ACTIVITY OF IONS.

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The view that chemical reaction in the electric discharge is conditioned by the chemical activity of atomic, or molecular, charged particles has been based mainly on three groups of experimental data: (1) the similarity between reaction caused by an electric discharge and

that initiated by α -particles,¹ and the proportionality, in the latter case, between the amount of chemical change and of ionisation (constancy of the M/N ratio),² (2) the correspondence in electron beam experiments between the critical energy for chemical change and that for the onset of ionisation, and (3) the general character of discharge reaction and the proportionality between the current carried in a glow discharge and the rate of chemical reaction in it.^{3, 4, 5, 6}

The aim of this paper is to review the subject in the light of the statistical theory of Part I.; for whilst certain optically allowed transitions lead to ionisation, and, as effected by electron impact, might therefore account, in some cases at least, for (3) above, there are a number of cases in which it appears more probable that discharge reaction is attributable mainly to the uncharged products of collisions between electrons and the reactant molecules.

1. The Data for Reaction Initiated by α -Particles.

The facts stated in (1) above would lead to the conclusion that ions are responsible for the observed reaction were it not known, as pointed out by Rutherford, Chadwick and Ellis,⁷ that, in molecular gases, less than half the energy of α -particles is used in effecting ionisation. Evidence for the occurrence of excitation along α -particle tracks has long been available^{8, 9}. Since it is known from photo-chemical experiments that excitation processes frequently lead to products which initiate reaction, it may not be necessary to look further than these for an explanation of α -particle reaction, as Emeléus and Lunt,¹⁰ and more recently, Eyring, Hirschfelder and Taylor¹¹ have surmised.

2. The Data of Electron Beam Experiments.

The technique of electron beam experiments to determine the least electron energy for which reaction occurs is essentially the same as that for determining the critical energy for excitation and ionisation.¹² But the chemical experiments are beset with considerable additional difficulties which arise from the comparative insensitivity of chemical,

¹ Lind and others, *Trans. Am. Elec. Chem. Soc.*, 1927, **52**, 37; *J.A.C.S.*, 1928, **50**, 1767; 1929, **51**, 365 and 2811; 1930, **52**, 4450; *Trans. Am. Elec. Chem. Soc.*, 1931, **59**, 159, 165.

² Lind, *The Chemical Effects of α -Particles*, 2nd ed., New York, 1928; *Science*, 1928, **67**, 656; *Chemical Reviews*, 1930, **7**, 203.

³ Guntherschulze, *Z. Elektrochem.*, 1924, **30**, 637.

⁴ Finch and others, *Proc. Roy. Soc., A*, 1926, **111**, 257; 1927, **116**, 529; 1929, **124**, 303 and 532; 1930, **129**, 656; 1931, **133**, 173; 1934, **143**, 482; *J.C.S.*, 1935, 32.

⁵ Brewer and others, *J. Physic. Chem.*, 1929, **33**, 883; 1930, **34**, 153, 554, 1280, 2343; 1931, **35**, 1281, 1293; 1932, **36**, 2133, 2395; 1933, **37**, 889, 897; 1935, **39**, 889.

⁶ Kirkby, *Proc. Roy. Soc., A*, 1911, **85**, 151.

⁷ Rutherford, Chadwick and Ellis, *Radiations from Radioactive Substances*, Cambridge, 1930.

⁸ Sir William and Lady Huggins, *Proc. Roy. Soc., A*, 1903, **72**, 196, 409; 1905, **76**, 488; 1905 **77**, 130.

⁹ Hinstedt and Meyer, *Physikal. Z.*, 1905, **6**, 688; 1906, **7**, 672; Walter, *Ann. Physik*, 1905, **17**, 367; 1906, **20**, 327; Pohl, *Ann. Physik*, 1905, **17**, 373; 1906, **18**, 406; Bosch, *Arch. Neerl.*, 1925, **8**, 163.

¹⁰ Emeléus and Lunt, *Nature*, 1936, **137**, 404.

¹¹ Eyring, Hirschfelder and Taylor, *J. Chem. Physics*, 1936, **4**, 479 and 570.

¹² Franck and Jordan, *Anregung von Quantensprünge durch Stösse*, Leipzig, 1926; Penning and de Groot, *Handb. Physik*, 1933, 23/1.

compared with physical, methods for the detection of the onset of the formation of a new molecular or atomic species in the gas.

At the time when the critical energies for reaction were determined it was found in some systems that this critical energy was identical with the then accepted value of the critical energy for the ionisation of one of the reactants; such identity led naturally to the conclusion that the reaction was initiated by the ions formed at this critical energy. This identity no longer holds for the more recent and precise determinations of the critical energy for ionisation. Thus, for example, the values attributed to the critical energy for reaction in mixtures of (a) hydrogen and nitrogen,¹³ (b) hydrogen and carbon monoxide,¹⁴ and (c) nitrogen and oxygen,¹⁵ are, in each case, at least 1 el.-v. *above* the accepted critical energies^{16, 16(a)} for the simple ionisation of the reactants. In these cases, it is clear that the presence of the ions of both components is inadequate to initiate reaction. In other cases, for example, in hydrogen¹⁷ and in oxygen¹⁸ the values found for the critical energy for reaction, or chemical change, is definitely lower than that for simple ionisation,¹⁶ and may be identified with a critical energy for excitation as determined, for example, from spectroscopic data.^{16(a), 19} There is thus no evidence from electron beam experiments for the initiation of chemical change by ions; on the other hand they afford definite evidence that the products of excitation processes cause reaction.

3. The Data for Discharge Reaction.

Since Brewer⁵ has contributed the widest array of data for reaction in the glow discharge, and has been a most emphatic supporter of the ion reaction mechanism hypothesis, his views will be discussed here although similar conclusions have been reached by others.

An explanation has been sought for the constancy of the current efficiency in the negative glow, β_p , α , by considering the ionisation produced in the negative zones as equivalent to that produced by a flow of electrons, numerically equal to the current carried by the discharge, and having initial energy given by the cathode fall in potential. Linder's²⁰ more precise analysis of the régime in the negative zones, later amplified by Emeléus and Kennedy,²¹ shows that Brewer's model of the negative zones is too incomplete to warrant further discussion.

Both excited atoms and molecules have been excluded from possible reaction mechanisms because the intensity of light emitted by them in a glow discharge, considered as a function of pressure, is apparently unconnected with the rate of chemical reaction; this is to be expected because, for normal excited states, having a life-time of 10^{-9} — 10^{-7} sec.

¹³ Andersen, *Z. Physik*, 1922, 10, 54; Storch and Olsen, *J.A.C.S.*, 1923, 45, 1605; 1926, 48, 1298; Carross and Rideal, *Proc. Roy. Soc., A*, 1927, 115, 684; Brett, *ibid.*, 1930, 129, 319.

¹⁴ Carross and Rideal, *ibid.*, 127, 511.

¹⁵ Wansborough-Jones, *ibid.*; Henry, *Bull. Soc. Chim. Belg.*, 1931, 40, 371.

¹⁶ Knoll-Ollendorf-Rompe, *Gasentladungstabellen*, Berlin, 1935.

^{16(a)} Sponer, *Molekülspektren*, Berlin, 1935, and refs. given there.

¹⁷ Glockler and Thomas, *J.A.C.S.*, 1935, 57, 2357; Glockler, Baxter and Dalton, *ibid.*, 1927, 49, 58.

¹⁸ Henry, *Bull. Soc. Chim., Belg.*, 1931, 40, 305, 339; Glockler and Wilson, *J.A.C.S.*, 1932, 54; Dalton *J.A.C.S.*, 1929, 51, 2366.

¹⁹ Mulliken, *Rev. Mod. Physics*, 1932, 4, 1.

²⁰ Linder, *Physic. Rev.*, 1931, 38, 679.

²¹ Emeléus and Kennedy, *Phil. Mag.*, 1934, 18, 874.

radiation will occur before collision for the pressure range in Brewer's experiments. But, of course, this consideration does not exclude unexcited atoms, or metastable atoms and molecules, all of which may be the products of excitation processes.

Atoms, or other fragments, resulting from the dissociation of electronically excited molecules have also been excluded because there is no maximum in the reaction rate corresponding to the conditions in which atoms or fragments may most easily be extracted from a discharge. The equilibrium concentration of atoms, or other fragments, is, however, determined by the rate of their production and the rate of their destruction by chemical reaction, including the reformation of the molecules from which they were formed; hence, in the absence of auxiliary data, no simple relation is predictable between the stationary concentration of such fragments and the rate of formation of the final product of a discharge reaction.

The exclusion of the above mentioned uncharged products of electron collision with reactant molecules, which is now seen to be almost certainly unwarranted, led naturally to the view that the explanation for the observed reaction must be sought in terms of the charged products of such collisions. In further support of this conclusion, Brewer called attention to the sharply defined bands of reaction product that are observed on those portions of the walls of the reaction vessel, when suitable refrigerated, that enclose the regions of most intense ionisation, the positive column and of the negative glow;²⁰ these regions, are, however, also those in which the concentrations of excited atoms and molecules are greatest.²⁰ Similar deposits have been observed by Banerji and Ganguli²¹ whose work appears to show that they arise from the neutralisation of the random positive ion current at the walls. Furthermore, the existence of the so-called "ion-exchange" reactions of Kallmann and Rosen²² at once affords a possible explanation of these phenomena because, in many cases, the ionisation potential of the "product" molecules is lower than that of any of the reactants, and the pressure is so high that a "product" molecule produced in the gas phase could make a number of collisions with ions of the reactant molecules before reaching the walls.

Brewer has also supposed that the ions of the reactant molecules may initiate reaction when they reach the walls, the energy of ion recombination being available for dissociating either the recombined ion or some neighbouring molecules, or for providing part of the activation energy in reactions involving the neutralised ion. Apart from the lack of direct evidence for such processes, discussed in § 4, it appears likely that even if wall (or other surface) recombination were followed by dissociation, the resulting fragments, if atomic, would be preferentially adsorbed, and subsequently recombine with like fragments reforming the molecules from which they were produced; a considerable part of the energy released in the ion recombination would thus appear finally as heat conveyed to the walls, which the view generally accepted.²⁴ It is interesting to note that, for the formation of ammonia from nitrogen-hydrogen mixtures, Brewer himself reported data⁶ for the dependence of the rate of synthesis on the relative area of the anode and cathode, and which affords a strong indication that the ions reaching the cathode,

²⁰ Banerji and Ganguli, *Phil. Mag.*, 1933, 15, 676; 1934, 17, 313.

²¹ Smyth, *Rev. Mod. Physics*, 1931, 3, 347.

²⁴ See, for example, Compton and Langmuir, *ibid.*, 1930, 2, 191.

and recombining there, do not contribute appreciably to the observed reaction.

There is thus no evidence from the data for discharge reaction that charged particles are essential to the initiation, or to any other step, of the mechanism by which reaction occurs.

4. The Reactivity of Ions.

There are two main ways in which it has been supposed that charged molecular or atomic particles can cause chemical reaction: firstly, the energy liberated in the recombination of a positive ion with an electron, or negative ion, may be available to dissociate or activate the recombined ion, or some other particle with which it is in collision during the recombination process; secondly, an ion may have a specific chemical reactivity analogous to that of neutral molecules, atoms, and free radicals.

4.1. The Energy Liberated in Ion Recombination.

Since the disposal of this energy at the surface of a discharge tube has already been discussed, it remains to consider processes occurring in the gas phase. For simplicity the argument will be restricted to diatomic molecules and molecular ions, although it will be seen that it can readily be extended to more complicated cases.

In the recombination of an electron with a diatomic ion AB^+ (where A may be identical with B), the condition for the formation of a stable molecule, AB , is that energy equal to the sum of the energy of ionisation of AB , I_0 , and the kinetic energy of the electron, I_k must be radiated (or transferred to a third body) in the life-period of the ion-electron collision complex. This life-period may be roughly estimated as the time an electron spends in crossing a molecular diameter, 10^{-8} cm.; for an electron of velocity about 10^7 cms. sec.⁻¹, or of energy about 0.04 e.v., this time is about 10^{-15} sec., and would be correspondingly smaller for electrons of greater energy. Since no selection rules are contravened in the radiative process, the transition probability (the Einstein " A " coefficient) may be taken to be that of a normal allowed transition, about 10^8 sec.⁻¹; it follows that the probability of stable molecule formation is of the order of $10^{-15} \times 10^8 = 10^{-7}$ in a single collision. Whilst no recombination spectra are known for molecules, the values of this probability for atoms, deduced from the absolute intensity of the recombination spectra,²⁴ confirms the above rough estimate, and establishes that gas phase recombination by the emission of radiation is an extremely rare process, a conclusion in agreement with that reached from purely electrical considerations.²⁴ In molecular ions there is, however, the additional possibility that the energy released in recombination might be transferred to the internal motions of the molecule in the ground state and thus cause dissociation, or at least considerable activation. Such a process would be equivalent to the transfer of electron kinetic energy to molecular vibration (and rotation), processes known to be of low probability both from experiment,²⁵ and from theoretical considerations.²⁶ Thus, whilst the available energy

²⁴ Bailey and others, *Phil. Mag.*, 1923, **46**, 213; 1925, **50**, 825; 1928, **6**, 1073; 1930, **10**, 145; 1932, **13**, 993; Harries, *Z. Physik*, 1927, **42**, 26; Rammen, *ibid.*, 1931, **70**, 353.

²⁵ Mott and Massey, *The Theory of Atomic Collisions*, Oxford, 1933, 217; Bloch and Bradbury, *Physic. Rev.*, 1935, **48**, 689.

would be more than sufficient to cause dissociation in many cases, the low probability limits such decomposition to the class of very infrequent processes.

We now consider the case where the energy of (molecular) ion recombination is available for production of an excited molecular state of the recombined ion, a particular case arising when the transition occurs at such an internuclear distance that dissociation follows. The argument here follows that of Massey and Smith²⁷ for dissociation consequent upon electron attachment: if we consider, as before, a collision between an electron of energy V_k and an ion AB^+ in its lowest vibrational state,* it can at once be seen that the collision complex is indistinguishable from the neutral molecule AB in which the internuclear distance, by the Franck-Condon principle, is the equilibrium internuclear distance of the ion AB^+ (which we shall denote by r_+), and containing energy $V_i + V_k$. If now there happens to be an excited state of AB such that at the internuclear distance r_+ , its energy, relative to the ground state, is nearly† equal to $V_i + V_k$, the systems will be in resonance and transitions to the excited state of AB will occur. But, even if there happens to be a suitable excited state, the systems will be in resonance only for electrons having energy very close to V_k ; it has been seen in Part I. that in the negative glow and the positive column the electrons have an energy distribution, and therefore but a very small fraction of the total electrons present may have energy close to V_k , with the result that in either of these discharge zones the process may be a very infrequent one. The simplest variant of this process is that a third molecule, CD , is present during the collision and that this molecule is activated or dissociated by absorbing the energy liberated in the recombination of the ion. In this case, too, the probability of energy transfer would be appreciable only if there were a level in CD in resonance with the available energy, $V_i + V_k$. The infrequency of ternary collisions at the low pressures used in most discharges, the low relative concentrations of ions and electrons,²⁸ and the possibility that only a small fraction of the electrons have energy close²⁹ to V_k , are three factors all tending to restrict such collisions (even if every one of these leads to activation or dissociation) to the class of very infrequent processes, considerably inferior in rate to the observed rates of chemical reaction in discharges.

The next type of process to be considered is that in which an ion, AB^+ , captures an electron from another molecule CD in a collision; the energy liberated is then the difference between the ionisation energy of AB and that of CD , a quantity which will be denoted by V_0 . By the Franck-Condon principle, if such an electron transfer occurs the resulting new ion, CD^+ , would be produced at the internuclear distance of the neutral molecule CD , r_0'' ; the process will occur with appreciable probability only if there happens to be an excited state of CD^+ such that at the internuclear distance r_0'' its energy relative to that of the normal state

²⁷ Massey and Smith, *Proc. Roy. Soc., A*, 1936, 155, 472.

* The lowest vibrational state is considered because, in most of the discharge conditions of present interest, the majority of ions are probably in this state; the argument is, however, easily extended to higher vibrational states.

† The order of the energy discrepancy will be 1 e.v. since this must be same as that due to the change of internuclear distance in a transition between different electronic states.²⁸

²⁸ Stueckelberg, *Physic. Rev.*, 1932, 42, 518.

²⁹ Darrow, *Electrical Phenomena in Gases*, Baltimore, 1932.

of CD^+ is nearly * equal to V_0 , for then the systems will be in resonance. The best known example of such an ion reaction is afforded by the work of Smyth and Stueckelberg³⁰ on collisions between Ne^+ ions and normal oxygen molecules. In this case it happens that the energy acquired by the excited ion, O_2^+ , is greater than the dissociation energy, and it therefore dissociates spontaneously into O and O^+ . Apart from the restriction implicit in the necessity for there being an excited state of CD^+ in resonance with V_0 , the low pressures and low concentrations of ions in most discharges of present interest limit the maximum possible rates of such processes to comparatively low values.

The last type of collision process we consider is that between a positive ion and a negative ion: this is most simply treated as a variant of the previous case in which the collision complex of CD^- and AB^+ may be regarded, after electron transfer has occurred, as composed of AB and CD in which the internuclear distances are, respectively, the equilibrium internuclear distances of the ions from which they are derived; the complex as a whole then contains the energy $V'_0 = V_i - V_{0-}$, where V_i has the same significance as in the previous cases, and V_{0-} denotes the ionisation energy of CD^- . The reaction which will then occur is that for which the sum of the energies of the excited states of CD and AB is most closely in resonance with the available energy, V'_0 ; in general this will occur with CD in an excited vibrational level of the ground electronic state, and with AB in some vibrationally excited upper electronic state. Furthermore, since V_{0-} is likely to be small † compared with V_0 and since there are numerous upper electronic states with energies lying close to V_i (in any molecule), it is probable that the excited states necessary for resonance with V'_0 exist in most cases; the electronically excited state of AB must then, if it is stable, lose its energy by radiation, or, if unstable, dissociate. Whilst the rate of recombination of ions of opposite sign has been the subject of many investigations, no observation of the radiation consequent on this has been reported. The observed rate of recombination is remarkably high, being at atmospheric pressure approximately 10^4 that of the bi-molecular collision rate of the corresponding neutral particles: recombination may therefore be of importance in connection with chemical reaction in discharges because, as seen above, the energy liberated may cause dissociation, or lead to the emission of radiation which might be absorbed by the other molecules present. On the other hand, there are few discharges of present interest for which there is evidence of the existence of negative ions in concentrations exceeding a very small fraction of that of the positive ions.

Summarising this discussion, it is seen that in all cases the likelihood of processes occurring in which the energy of recombination may become available for chemical reaction depends on the existence of excited states of ions and of neutral molecules satisfying certain particular energy requirements. Any particular case must therefore be considered on its merits, but in the present somewhat scanty state of

* That is, within about 1 e.v.

³⁰ Stueckelberg and Smyth, *Physic. Rev.*, 1928, 32, 779; Stueckelberg, *ibid.*, 1929, 34, 65.

† For example, the energy of electron attachment to an oxygen molecule³¹ is about 0.1 e.v.; the energy of detachment is probably of the same order of magnitude.

³¹ Loeb, *Physic. Rev.*, 1933, 43, 6.

our knowledge of the higher electronically excited states of molecules, it is only in a few cases that the problem can be adequately discussed. Apart from this restriction, in the case of ion-electron collisions, there is also a restriction to a very narrow range of electron energies. The two remaining processes either require ternary collisions, or involve a particle of a type which exists in most discharges of interest at relatively low concentrations only. It is therefore reasonable to suppose that in most discharge reactions none of these processes is operative unless there is special evidence to the contrary.

4.2. The "Chemical" Reactivity of Ions.

Although it has been frequently postulated that chemical rearrangement may take place as a result of collisions between charged and uncharged molecules, there is only one known case of charged particles effecting reaction when these have kinetic energy of the same low order as is possessed by molecular ions in discharges in which chemical reaction has been examined. This is the reaction $H_2 + H_3^+ = H_3^+ + H$, the occurrence of which was established by Dorsch and Kallmann;³² the fact that detectable amounts of atomic hydrogen were formed, despite the small concentrations of H_3^+ ions present, suggests that the energy of activation is small and the velocity constant large, in agreement with calculations based on wave mechanical theory.^{33, 11}

Direct investigation by the use of ion beams is beset with difficulties similar to those encountered in working with electron beams (see § 2); whilst there are considerable discrepancies between the results of different investigators,^{10(a)} it is clear that the critical energy for reaction as effected by ion beams is at least about 20-30 e.v., and thus vastly in excess of the mean energy of ions in many discharges³⁰ causing chemical reaction. Even larger values of critical (ion) energy are found for electronic excitation by ion beams,³⁴ and wave mechanical theory predicts that no appreciable excitation will occur until the ion energy is considerably in excess of that necessary to effect the excitation process itself.³⁵

It is true that the rate at which ions collide with neutral reactant molecules to give chemically new products may be discussed in terms of expression (3), Part I, when n_e is replaced by the ion concentration, n_+ , when V denotes the kinetic energy of a colliding ion, $Q(V)$ the probability cross-section (in units of πa_0^2) for a specified collision process, $f(V)$ the energy distribution function for the ions, and when k is replaced by $4.37 \times 10^8 \times a$, where a is the ratio of the mass of the ion to that of a hydrogen atom. But since the current carried by a discharge cannot usually be expressed in terms of the drift velocity of the ions, it is usually not possible to derive from this modified form of expression (3) expressions for the current and energy efficiencies of such ion collisions which have properties similar to those of the corresponding quantities as observed for reaction in discharges. This result is not in itself sufficient to exclude the possibility that ions initiate reaction in discharges; but since $f(V)$ is appreciable only for V less than 1 e.v., in the

³² Dorsch and Kallmann, *Z. Physik*, 1925, 28, 452.

³³ Coulson, *Proc. Camb. Phil. Soc.*, 1935, 31, 244; Eyring, Rosen and Hirschfelder, *J. Chem. Physics*, 1936, 4, 121.

³⁴ Kirschstein, *Z. Physik*, 1930, 60, 184; Appleyard, *Proc. Roy. Soc., A*, 1930, 128, 330.

positive column and the negative glow,²⁰ and if, as seems likely^{10(a), 24} from experiment, $Q(V)$ is zero for V less than about 20 e.v., it follows that the overlap between $Q(V)$ and $f(V)$ and, hence, the rate of collision, must be extremely small. By evaluating the integral in this modified expression (3) for any likely values of $Q(V)$ and $f(V)$, it is easy to show that the resulting value for the rate is, by many powers of ten, inferior to the rate of reaction frequently observed in discharge reaction. In such cases it would be necessary to suppose that each ion-reactant collision ultimately gives rise to the formation of a correspondingly large number of molecules of the final product; in most cases such a possibility, is, of course, excluded.

Concerning the activation energy of collisions leading to chemical rearrangement between molecular ions and molecules having comparable kinetic energy very little is known. There is no reason to suppose from the scattering of molecular ion beams in molecular gases that the rate of transfer of kinetic into vibrational energy is significantly different from that of the corresponding neutral particles. By neglecting the effects arising from the charges on the particles, estimates of the activation energy may be derived by considering the heats of dissociation, equilibrium internuclear distances, and molecular diameters, of the colliding particles according to the method discussed by Franck and Rabinowitch;²⁵ this procedure leads obviously to activation energies of the same order as those for thermal reaction between neutral molecules, 1.5-2.5 electron-volts. In one case only, the reaction $H_3^+ + H_2 = H_3 + H$, has the problem been approached from wave mechanical theory:^{26, 27} Eyring concludes²⁸ that the activation energy is small, but although this result conflicts with the prediction from the Franck-Rabinowitch rule, no general conclusion can be drawn from this single application of wave mechanical theory.

Summarising this discussion of ion reactivity, firstly, it must be emphasised that there is only one example known for which there is direct evidence, and this is purely qualitative. Secondly, whilst in this one case (for which alone the necessary calculations have been performed) the wave mechanical analysis of the problem predicts a low activation energy, there is no indication from scattering experiments that the same may be true for other (postulated) cases; moreover, by analogy with thermal reactions between neutral particles, it may be anticipated that the activation energy will not be very small. Thirdly, the absence of fast moving ions in discharges excludes the possibility that electronic excitation by ions occurs in these. Whilst it is necessary to consider any particular case on its merits, it is thus seen to be improbable that any reaction in a discharge at temperatures not greatly exceeding 300° K. can be attributed to the chemical reactivity of the ions present.

5. Conclusions and Summary.

The following conclusions are reached from the preceding discussion of the various aspects of the hypothesis that the chemical reactions occurring when a discharge passes through a gas are attributable to the ions present. *Firstly*, the analogies presented by reactions due to α -particles do not support this hypothesis since they themselves are probably due to the excitation caused by the α -particles. *Secondly*, the data for critical potentials for electron beams indicate that these

²⁵ Franck and Rabinowitch, *Z. Elektrochem.*, 1930, 36, 794.

are below the ionisation potentials of the reactant molecules. *Thirdly*, the arguments which have been advanced from the general character of discharge reactions have been shown to be inconclusive. *Fourthly*, collision processes in which the energy of ion recombination may become available for initiating reaction have been shown to belong to a class of infrequent events for the conditions obtaining in glow discharges; a possible exception is the case of recombination between ions of opposite sign, but there is little evidence for the existence of negative molecular ions in significant concentration in many discharges in which chemical reaction has been studied. *Lastly*, there is only one example known for which there is direct evidence of the chemical reactivity of an ion of low kinetic energy; there is no evidence from scattering experiments for many of the other cases which have been postulated.

Thus, whilst no categorical statement is possible, and indeed any particular case must be considered on its merits, there are seen to be many reasons for believing that chemical reaction in discharges is unlikely to be attributable to the ions there present.

To Dr. H. S. W. Massey the author wishes to express his deep indebtedness for many suggestions, and for the numerous opportunities afforded him for discussing the problems raised in this paper, particularly those in Section 4.

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THE RAMAN SPECTRUM OF DEUTERO-SULPHURIC ACID.

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The Raman spectrum of sulphuric acid has been very thoroughly investigated,¹ and the lines in the spectra of the pure acid and its solutions in water have been simply explained on the basis of successive dissociation of the $\text{SO}_3(\text{OH})_2$ molecule into H^+ , HSO_4^- , and SO_4^{2-} ions. There is, however, a definite shift in many of the lines on dilution of the acid, and this shift is too large to be entirely explained by assuming that it is due to changes in intermolecular forces. Woodward and Horner² from a careful study of microphotometer curves suggest that the broad lines whose frequencies vary can be analysed into narrow components of constant frequency, characteristic of the different molecular or ionic species present. Rao³ had also put forward a similar suggestion, comparing the spectra of pure H_2SO_4 and KHSO_4 . On the other hand Bell and Jeppesen,⁴ after experiments performed over a very wide range of dilutions, could find no trace of separate

¹ For references see Angus and Leckie, *Proc. Roy. Soc., A*, 1935, 149, 327.

² *Proc. Roy. Soc., A*, 1934, 144, 129.

³ *Ind. J. Physics*, 1933, 8, 123.

⁴ *J. Chem. Physics*, 1935, 3, 245.

components on their microphotometer curves, and obtained evidence for a gradual shift.

The chief difficulty is that the breadth of the H_2SO_4 lines, and the presence of a relatively strong continuous background in the spectrum, renders the usual analysis by microphotometer curves taken under high dispersion of little value. If, however, the hydrogen in sulphuric acid is replaced by deuterium, the lines due to $\text{SO}_3(\text{OH})_2$ should show a definite isotope shift, those due to the HSO_4^- ion a smaller shift, whilst those due to the SO_4^{--} ion should be unaltered in frequency. Then, if the dilution shifts are due to the changing intensity of different components of the broad lines of the Raman spectrum, they should be appreciably different in H_2SO_4 and D_2SO_4 .

The spectrum of D_2SO_4 is also of interest in connection with the general isotope effect in spectra. Deuterium substitution in acetic acid has been studied by Angus, Leckie, and Wilson⁵ and Engler,⁶ and the frequencies of the lines in the spectrum of CH_3COOD are in many cases intermediate in numerical value between the corresponding values in CH_3COOH and CD_3COOD . This is particularly marked in the lower frequencies which almost certainly arise in parts of the molecule well removed from the point of substitution, and in which one would expect almost the same value in CH_3COOH and CH_3COOD . This result was kept in mind during the examination of D_2SO_4 , but the isotope shift in this substance is much smaller, and of the expected order.

Experimental.

The D_2SO_4 was prepared by the interaction of SO_2 and 99.6 per cent. D_2O . The small amount of residual protium present cannot have any appreciable effect on the Raman spectrum. SO_2 was distilled *in vacuo* from oleum into a glass vessel until a known weight of pure SO_2 was obtained. This SO_2 was distilled directly into the theoretical weight of D_2O so as to produce 100 per cent D_2SO_4 ; the reaction proceeded smoothly at 0°C . In preliminary runs it was found that a very small quantity of residue, which could not be distilled over, remained in the SO_2 vessel after the distillation; allowance was made for this in weighing the theoretically equivalent quantities.

The Raman spectra were obtained with the apparatus previously employed,⁴ using a dispersion of 20 Å/mm. at 4600 Å. 1.6 c.c. of 100 per cent. D_2SO_4 was placed in the Raman tube and its spectrum obtained. D_2O was added in stages to obtain the spectra of the acid at different concentrations. These concentrations, calculated from the amount of D_2O added, were not known to more than about 5 per cent. accuracy, but as the spectrum was not sensitive to such a concentration change it was considered unnecessary to make an accurate analysis at each dilution. Exposures of from 6 to 70 hours were given. For most of the plates the 4047 Å line was filtered out with sodium nitrite solution, some, however, were taken with unfiltered light, or with the 4047 Å line using an iodine filter. A fairly strong continuous background was present in all the spectra, and most of the Raman lines were rather diffuse. By taking the mean of from 5 to 10 sets of lines for each strength of acid the frequencies of most were obtained to within an error of $\pm 3\text{ cm}^{-1}$, but for the weakest lines the error is about $\pm 10\text{ cm}^{-1}$. The approximate intensity of each line is denoted as (s)-strong, (m)-medium and (f)-faint.

⁵ *Proc. Roy. Soc., A*, 1936, 155, 183.

⁶ *Z. physik. Chem., B*, 1936, 32, 471.

Results.

In Table I. the frequencies (in cm.^{-1}) of the Raman lines of D_2SO_4 are compared directly with the corresponding values for H_2SO_4 obtained by previous investigators.

In D_2SO_4 line (a) was weaker than the corresponding line in H_2SO_4 , and could not be resolved. Also, the absence of line (e) in the spectrum of the "heavy" acid is not significant, as in H_2SO_4 it is faint and not universally reported, although it has certainly real existence. The presence of line (f) in the 100 per cent. D_2SO_4 spectrum shows that a trace of D_2O was present. A very small amount of water suffices to make this line very strong in the spectrum of H_2SO_4 , so its appearance here is clearly due to difficulty in distilling exactly equivalent quantities of D_2O and SO_3 in the preparation. Lines (g), (h), and (i) were very faint and difficult to measure accurately. Most authors on H_2SO_4 quote (g) and (h) together as a fairly strong, single line, but there is considerable discrepancy in the published

values, and the presence of two lines in D_2SO_4 indicates that Woodward and Horner, and Bell and Jeppesen are correct in reporting two lines here. The only lines showing a definite isotope shift are (b), (c), and (d); these shifts are discussed later. The apparent shifts in (g), (h), and (i) are all within experimental error.

Table II. gives the values found for D_2SO_4 at different concentrations in D_2O , and the corresponding figures for H_2SO_4 . Considering the number

TABLE I.

H_2SO_4	D_2SO_4	
387 (f)	412 (f)	a
424 (m)		
560 (m)	550 (m)	b
741 (f)	711 (f)	c
913 (s)	902 (s)	d
975 (f)	—	e
—	1050 (s)	f
1140 (m)	1133 (f)	g
1195 (f)	1192 (f)	h
1360 (f)	1330 (f)	i

TABLE II.

Vol. Per Cent.	100.	85.	75.	50.	25.	10.
D_2SO_4.						
a	405 (f)	414 (f)	412 (f)	428 (f)	437 (f)	—
b	550 (m)	558 (m)	591 (m)	590 (m)	585 (m)	602 (f)
c	711 (f)	711 (f)	—	—	—	—
d	902 (s)	903 (s)	903 (m)	898 (m)	896 (f)	896 (f)
e	—	—	—	983 (f)	989 (m)	986 (f)
f	1050 (s)	1048 (s)	1047 (s)	1048 (s)	1050 (s)	1051 (m)
g	1133 (f)	1125 (f)	1140 (f)	1160 (f)	1155 (f)	—
h	1192 (f)	1250 (f)	1250 (f)	1228 (f)	1244 (f)	—
i	1330 (f)	1319 (f)	—	1345 (f)	1361 (f)	—
H_2SO_4.						
a	387 (f)	412 (m)	419 (m)	422 (m)	423 (m)	432 (m)
b	424 (m)	—	—	—	—	—
c	560 (m)	571 (m)	576 (m)	585 (m)	590 (m)	602 (m)
d	741 (f)	—	—	—	—	—
e	913 (s)	909 (s)	907 (m)	901 (m)	894 (f)	895 (f)
f	975 (f)	972 (f)	—	984 (f)	982 (m)	985 (m)
g	—	1038 (s)	1035 (s)	1039 (s)	1045 (s)	1047 (s)
h	1140 (m)	1151 (f)	1157 (f)	1172 (f)	1168 (f)	—
i	1195 (f)	—	1216 (f)	1234 (f)	1233 (f)	—
i	1360 (f)	1323 (f)	1327 (f)	1341 (f)	1337 (f)	—

of investigations that has been made on H_2SO_4 , the agreement between published results is not good, and in Tables I. and II. the most probable values, obtained by comparing as far as possible all the data available, are given.

It is clear that the D_2SO_4 spectra show a dilution shift in exactly the same manner as H_2SO_4 . It is rather surprising that the bisulphate ion frequency (f) (about 1050 cm^{-1}) does not show any isotope effect—the values in the "heavy" acid are, in fact, slightly higher—and this anomaly will be discussed later. The general isotope effect is, as might be expected, quite small. As dilution progressed the D_2O band, centred at about 2510 cm^{-1} , appeared and became well defined at dilutions above 50 per cent., this corresponds to the behaviour of the water band in sulphuric acid.

Discussion.

The effect of successive dissociation of the sulphuric acid molecule into bisulphate and sulphate ions was evident in the earliest Raman investigations on this substance, and is the most prominent feature of the spectrum. In addition there are two points of interest—the dilution shift, and the effect of hydration of the acid on the spectrum. The explanation of the dilution shift advanced by Woodward and Horner covers the observed facts in a very satisfactory manner, yet since Bell and Jeppesen, from their extensive investigation, suggest that there is no evidence for the composite character of many of the lines the results from D_2SO_4 must be taken into consideration. Recently, also, Cartwright, in a study of the far infra-red spectrum ⁷ of H_2SO_4 , and Plyler and Williams, investigating the infra-red spectrum of heavy acid solutions, ⁸ have drawn attention to the probable association of the acid molecules with water. Cartwright suggests that the effect of adding water to sulphuric acid is first, the formation of some hydrated sulphuric acid $(\text{SO}_4)^{--}(\text{OH})_4^{++}$, then the formation of a hydrated bisulphate ion $(\text{H}_2\text{SO}_4)^-$, and finally sulphate ions $(\text{SO}_4)^{--}$; suggestions which must be kept in mind in a discussion of the Raman spectrum.

Considering the results for D_2SO_4 in more detail, it is seen that frequency (a) (about 410 cm^{-1}) increases in displacement with dilution in exactly the same way as in H_2SO_4 . Woodward and Horner attribute this increase in H_2SO_4 to the presence of three components, one of 381 cm^{-1} due to H_2SO_4 , a common frequency 417 cm^{-1} , and one of 452 cm^{-1} due to SO_4^{--} . On account of the faintness of the line in D_2SO_4 the actual frequency of the lower component of this line could not be determined. Measuring its breadth gave the lower limit of the line as 370 cm^{-1} , but this is not conclusive evidence that an isotope shift in the 381 cm^{-1} component has taken place. Such a shift would have confirmed the origin of this line in the undissociated molecule. The agreement in the values for dilute D_2SO_4 and H_2SO_4 does seem to prove, however, that part of this line is due to the SO_4^{--} ion. The value of 435 cm^{-1} in the spectra is intermediate between 415 cm^{-1} (characteristic of the $=\text{SO}_2$ group and found in chlorosulphonic acid and sulphuryl chloride) and 455 cm^{-1} (characteristic of sulphates) both of which would be unaffected by deuterium substitution. Similar remarks apply to (b) and (d) (lines at about 570 and 905 cm^{-1}). Here, and particularly with (d), there are definite isotope shifts in the concentrated acid but not in the dilute, thus affording direct

⁷ *J. Chem. Physics*, 1936, 4, 413.

⁸ *Ibid.*, p. 460.

evidence that these lines are composite and consist of parts attributable to separate origins in the different concentrations, one due to H_2SO_4 , and the other to one of the ions.

The line (c) has not been reported in many investigations of H_2SO_4 . There is a faint, but quite well-defined line at 711 cm^{-1} in D_2SO_4 , and it seems clear that this must correspond to the 741 cm^{-1} line in H_2SO_4 . Pai⁹ regards this line as characteristic of the undissociated molecule, and this assignment is probably correct since it appears only in the most concentrated acid and is appreciably shifted in D_2SO_4 .

Line (e), at about 980 cm^{-1} , appears in both the concentrated and more dilute acids, but not at moderate concentrations. It is very weak in H_2SO_4 , and owing to the rather more difficult experimental conditions was not visible in strong D_2SO_4 . Most authors reporting this line in the spectrum of the strong acid stress its distinct character, and state that it must not be confused with the strong SO_4^{--} line of the same value in the dilute solution. Yet, as Cartwright⁷ points out, there is every reason to assume the presence of the hydrate $(\text{SO}_4)^{--}(\text{OH})_2^{++}$ in sulphuric acid containing only a trace of water, therefore one would expect the characteristic sulphate ion frequency to appear faintly in the spectrum of the more concentrated acid. It is significant that Bell and Jeppesen, who seem to have worked with the most anhydrous acid (f.p. 10.3°), do not obtain this line from their 100 per cent. acid but find it appearing as soon as a small amount of water is added. In the circumstances one must assume that line (e) has the same origin throughout, *viz.*, the SO_4^{--} ion, and that its presence in the spectrum of concentrated H_2SO_4 confirms the presence of the ionic hydrate.

Line (f), the bisulphate ion frequency of 1050 cm^{-1} , is rather more difficult to explain, particularly since its value is not depressed in D_2SO_4 . Woodward and Horner consider that it exhibits a real dilution shift, but the experiments with the "heavy" acid, in which there is practically no dilution effect, indicate that the variations in H_2SO_4 have no real significance. Cartwright suggests that the bisulphate ion is hydrated in solution and is of the composition $(\text{H}_2\text{SO}_5)^-$, quoting in support of this view data obtained from freezing-point/composition and viscosity/composition curves. From the standpoint of the Raman spectrum the existence of such a hydrate is very doubtful, since one would then expect a real isotope shift instead of the observed zero effect. It seems most probable that the line (f) arises from a valency vibration involving only the oxygen atoms, and is thus closely related to the 985 cm^{-1} SO_4^{--} frequency, and the frequencies at approximately 1055 cm^{-1} in nitrates and carbonates.

Since it is difficult to obtain reasonable exact values for the three highest frequencies (g), (h), and (i), isotope or dilution effects cannot be verified. The results for D_2SO_4 do show that (g) and (h) are distinct, separate lines. Most investigators find that these lines become less intense as dilution proceeds, but in D_2SO_4 no appreciable variation in intensity was detected. Bell and Jeppesen alone observed this approximately constant intensity in H_2SO_4 . In the absence of more precise frequency data these lines cannot be definitely associated with any particular ion or group.

⁹ *Phil. Mag.*, 1935, 20, 621.

Summary.

The Raman spectrum of D_2SO_4 in the pure form, and at various concentrations in D_2O has been determined. Certain of the lines show small isotope shifts, together with frequency changes on dilution. By comparing these with the corresponding values in H_2SO_4 evidence is obtained in support of the view of Woodward and Horner that many of the lines are composite in character. The generally accepted assignments are reviewed from the standpoint of the results obtained for D_2SO_4 .

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THE ELECTROPHORETIC MOBILITY OF PURIFIED TRISTEARIN. PART I. THE ACID REGION, p_H 2 TO 7.

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In this paper measurements of the electrophoretic behaviour of dispersions of tristearin are described. It was desired to obtain a reproducible "inert" surface which could be subjected to a detailed examination as the basis of similar measurements on other long chain compounds. Tristearin is a naturally occurring fat which is not reactive and which might be expected to carry a higher charge than a hydrocarbon. The mobility has been examined in the presence of various salts. Particular care has been taken to ascertain the effect of the hydrogen ion concentration on the mobility. The work described has shown that over the range p_H 5 — 7, which includes that of "distilled" water, the mobility varies rapidly with p_H and hence, in attempting to find the effects of added salts, it is essential that the hydrogen ion concentration should be controlled as accurately as possible. The effect of p_H change would obviously be most marked with the alkali metal salts of weak acids and it seems that the significance of the p_H in the case of inert surfaces which owe their charge not inconsiderably to the hydroxyl ion has been frequently overlooked.

Experimental.

The electrophoresis measurements were carried out macroscopically in the apparatus described by Price and Lewis¹ using the moving boundary method, which has the advantage of accurate temperature control. The main U-tube, of quartz, 1 cm. in diameter, was fitted with side arms

¹ Price and Lewis, *Trans. Faraday Soc.*, 1933, **29**, 775.

of sufficient length to prevent the products of electrolysis from the working electrodes from migrating into the body of the apparatus during a determination. The main electrodes, an anode of zinc and a cathode of lead coated electrolytically with lead peroxide, eliminated gas evolution and its kindred disturbances.*

For measuring the potential gradient across the central part of the U-tube small platinum electrodes, which were quite reproducible, were introduced at either end of the main arms. The effective distance between these had been ascertained by conductivity measurements.

To determine the potential gradient across the main tube a known potential from a battery was put across the subsidiary electrodes and the potential in the tube was adjusted to be equal to this by varying the voltage between the outside electrodes. A balance method was employed to match the potentials, the null point being found with the aid of a capillary electrometer. It was necessary to reset the outside voltage at ten-minute intervals, or more frequently in acid solutions.

To eliminate disintegration or blurring of the boundaries through temperature variations, the tube was suspended in a glass trough of water, maintained within 0.1°C . of 25°C . by an efficient circulating system from a thermostat. All solutions and emulsions were also brought to 25.0°C . before introduction into the apparatus.

The boundaries were examined through a telescope placed 1 metre from the apparatus. On account of the thinness of the emulsions the tube was illuminated by a brilliant light placed obliquely at the rear of the trough.

The electrophoretic data obtained are accurate to approximately 4 per cent.

The p_H values were determined by the glass electrode at 25°C . in an oil thermostat. The gold-quinhydrone electrode was also utilised for some of the results in buffer solutions. The results obtained are accurate to 0.01 p_H unit for buffer solutions and for values below p_H 4 in unbuffered solutions. For unbuffered solutions the error is not greater than 0.05 unit up to p_H 5.5 or 0.1 unit above this value.

Purification of the Tristearin.

After a preliminary examination of several preparations, the fat employed was one specially prepared and kindly supplied by Messrs. Lever Bros. Ltd. This product was a smooth white odourless solid with an iodine value of 0.6. It contained a few per cent. of tripalmitin but was very free from acids or unsaturated compounds. It was further purified by dissolving 100 gm. in 300 ml. of pure boiling chloroform and allowing the solution to cool slowly. As soon as a fair crop of solid had been precipitated it was drained off and washed once with a little ice-cold chloroform. By removing the yield in small quantities the liability of the mother liquor being trapped in the solid was reduced to a minimum. The final separation of the fat was carried out by cooling in melting ice. The recrystallizations were continued until no further alteration in the product could be detected, the mobility of an emulsion made from each fraction in the presence of $N/100$ secondary sodium citrate being used as the criterion of electrophoretic purity. It was found that two recrystallizations of the first crops sufficed to give a product of constant mobility. The mobility, which at 20°C . was 11.6×10^{-8} cm./sec. under 1 volt/cm for the original substance, fell after two recrystallisations to the constant value of 7.6×10^{-8} . The final product was quite odourless and gave a colourless solution in chloroform. As a further precaution some of this

* For the measurements with ferrocyanide solutions the zinc electrode is inadmissible. It was replaced by a silver-silver nitrate electrode with a saturated ammonium nitrate bridge. Suitable precautions were taken to prevent the ammonium nitrate from entering the U-tube.

purified tristearin was recrystallised from "analar" acetone, which had been twice redistilled. The mobility of the fat was found to be unaffected.

Preparation of the Emulsions.

In the investigation of the various fractions obtained in the purification, the dispersions were made up in an identical manner by the addition of 0.6 gm. of fat, in 10 ml. of boiling alcohol, to one litre of distilled water at 75° C. This temperature was chosen because it is just above the melting-point of tristearin; below this temperature rapid solidification might produce the meta-stable α -form. 75° C., however, is below the boiling-point of the alcohol and hence there is approximately 1 per cent. of alcohol in the emulsions. It is possible that this might exert a noticeable effect on the mobility. Emulsions were therefore made up by adding the alcoholic solution of tristearin to water which was boiling vigorously. In this way the alcohol was almost completely driven off at the moment of contact with the water. Finally, a dispersion was boiled continuously for four hours, the evaporation losses being made up with distilled water, before being allowed to cool. In every case it was observed that the mobility was unaltered and hence the trace of alcohol has no measurable effect. All dispersions were allowed to stand overnight before buffering and using.

It follows from the fact that prolonged boiling has no effect that there is no aging effect in the tristearin emulsions. In practice it has been observed that mobility measurements made after one week are the same as those made after 24 hours.

(a) The Effect of p_H on Emulsions of the Purified Fat in Various Buffer Solutions.

The accuracy with which the mobility— p_H curve can be determined is, to a large extent, dependent upon the matching of the p_H of the emulsion and the clear liquid and upon the correct measurement of the various p_H values. It is, therefore, most convenient to carry out the determinations in buffered solutions and the effect of added electrolytes must be closely examined. For example, using a purified engine oil, Powis² found that at $N/100$ concentration of sodium chloride the mobility is almost the same as in the absence of any electrolyte, while Tuorila,³ working on a hydrocarbon, observed that at this concentration of

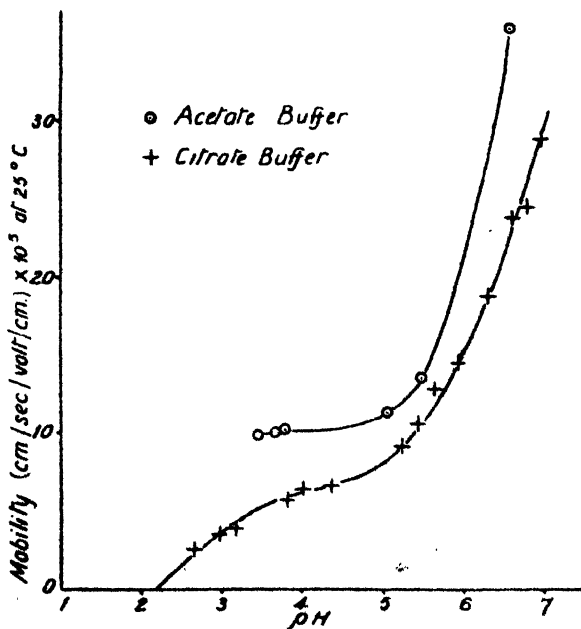


FIG. 1.—The mobility of Tristearin in Sodium Citrate and Acetate Buffers.

² Powis, *Z. physik. Chem.*, 1915, 89, 91.

³ Tuorila, *Kolloidchem. Beih.*, 1928, 27, 44.

sodium chloride the mobility had been reduced to about half that for electrolyte-free emulsions.

The buffers employed were citrate mixtures,

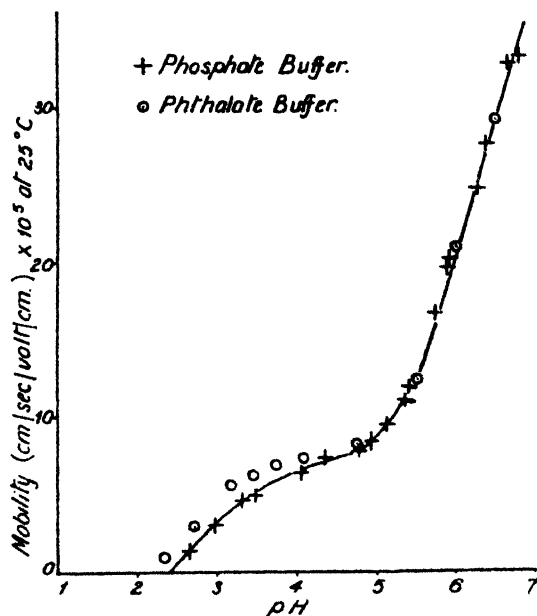


FIG. 2.—The mobility of Tristearin in Potassium Phosphate and Phthalate Buffers.

tained at a fixed concentration. The phosphate and phthalate buffers do not have this disability. A satisfactory degree of buffering with either of these substances is obtainable between p_H 3 and 7, while keeping the concentration of the alkali metal at $N/100$ throughout. For the higher p_H values, increasing amounts of the potassium salts were replaced by equivalent quantities of caustic soda whilst p_H 's below 4 were secured by the addition of small amounts of hydrochloric acid.

The supernatant liquid was in every case buffer solution of the same ionic composition as the dispersion. As the density of the dispersions is the same as that of the supernatant liquid it was found necessary for all emulsions to contain 2 per cent. of sucrose in order to obtain clear boundaries. This small amount of sugar has been shown by Northrop and Cullen⁴ to have a negligible effect upon the electrophoretic rate.

Table I. shows a typical example of a determination.

acetate-acetic acid solutions, and potassium phosphate and potassium phthalate solutions. The citrate used was that of Sørensen, diluted tenfold with emulsion or water as desired. The maximum concentration of sodium ion present was thus $N/50$ at p_H 5.2. The acetate solutions were adjusted to be $N/100$ with respect to the sodium acetate, the p_H being reduced by progressively replacing this salt with an equivalent amount of acetic acid. Both of these buffer systems suffer from the disadvantage that the concentration of the added salt is different at different p_H values. It is, however, not possible to cover a sufficiently wide p_H range if the sodium salt is main-

TABLE I.—COMPOSITION OF DISPERSION :
0.02 PER CENT. TRISTEARIN ; $N/100$
SØRENSEN'S CITRATE BUFFER ; 2 PER
CENT. SUCROSE.

Temp. 25.0° C. P.D. across centre tube
 p_H 5.67 60.0 volts. Current 2.1
milliamps.

Movement of boundaries (scale divs.) :

Time (mins.).	Cathode Limb (downwards).	Anode Limb (upwards).
0	0.0	0.0
10	3.25	3.25
20	6.5	6.5
30	9.75	10.0

Mean movement : 9.88 divisions in 30
mins. (1 scale division is 0.043 cm.)

Electrophoretic mobility under 1 volt/cm.
at 25° C. is 12.8×10^{-5} cm./sec.

⁴ Northrop and Cullen, *J. Gen. Physiol.*, 1922, 4, 635.

It will be seen from the mobility— p_H curves (Figs. I. and II.) in the presence of the different buffer solutions that the added electrolytes exhibit specific effects although the chief factor in determining the mobility is clearly the p_H value. In phosphate and phthalate solutions the mobility is the same for a given p_H value, except for the slight divergence at low p_H . In these two cases the amount of alkali metal salt present is the same throughout. This points to the possibility that in the case of these buffers the added anion is relatively unimportant compared with the effect arising from alteration in the concentration of the cation.

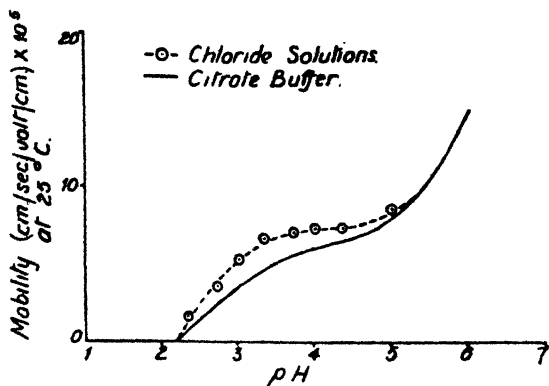


FIG. 3.—The mobility of Tristearin in N/100 Citrate Buffer, and the effect of replacing the Citrate ion by an equivalent amount of Chloride ion.

(b) The Effect of p_H on Tristearin Emulsions in the Presence of Sodium and Potassium Chlorides.

In order to obtain further information on the rôle played by the anion in the tristearin dispersions mobilities were also determined in sodium and potassium chlorides.

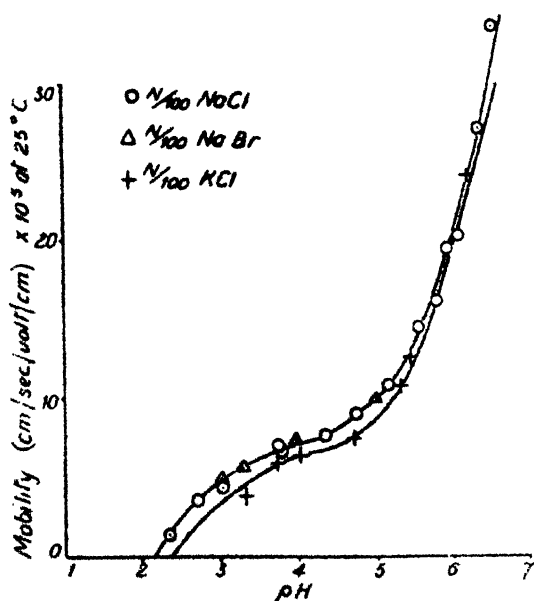


FIG. 4.—The mobility of Tristearin in N/100 Sodium and Potassium salts.

Fig. 3 shows mobilities in the presence of sodium chloride, the concentration of which was so arranged that the sodium ion concentration was the same as that in the citrate buffer at the same p_H value. The p_H values of the emulsions in the sodium chloride solutions have been attained by the addition of the appropriate quantities of hydrochloric acid. In the buffer solution the ions present are hydrogen, sodium, chloride and citrate, whilst in this case they are hydrogen, sodium and chloride. As the hydrogen and sodium are adjusted to be the same in both, the second case corre-

sponds effectively to the replacement of the citrate ion of the citrate buffered dispersions by the chloride ion. Fig. 3 illustrates the behaviour.

It will be noticed that, while the curves run together at p_H 5.2, in more acid solutions that for the emulsions buffered with citrate lies somewhat below the other.

Mobility measurements were also made using emulsions in which the concentration of added sodium chloride was kept at $N/100$ throughout, the p_H again being obtained by the addition of hydrochloric acid. A few similar points are shown for potassium chloride and sodium bromide. (See Fig. 4.)

It is seen that the points for $N/100$ potassium chloride and $N/100$ potassium phosphate buffer fall upon the same curve. In the same manner the mobility- p_H curves for $N/100$ sodium chloride and $N/100$ sodium bromide are identical. Moreover the curves in the presence of $N/100$ sodium salt lie somewhat above those for $N/100$ potassium salt. That the potassium ion has a rather greater discharging effect than the sodium ion under similar conditions has frequently been observed in the case of "inert" surfaces.⁶ The effect is always small. In the case of tristearin, whilst the steepness of the mobility- p_H curves above p_H 5 makes it difficult to distinguish between the sodium and potassium curves, below this value the difference appears to be roughly constant, being about one mobility unit.

The most striking conclusion to be drawn from the above results is the remarkable similarity in the effects of the different anions, particularly at the higher p_H values. It is not necessarily to be inferred from this behaviour in respect of mobility that the anions are without effect upon the charge density. This point is considered later.

(c) The Mobility of Tristearin at Constant p_H at Different Salt Concentrations.

In this section the effect of salts at different concentrations on the mobility of tristearin dispersions is recorded. Care has been taken to

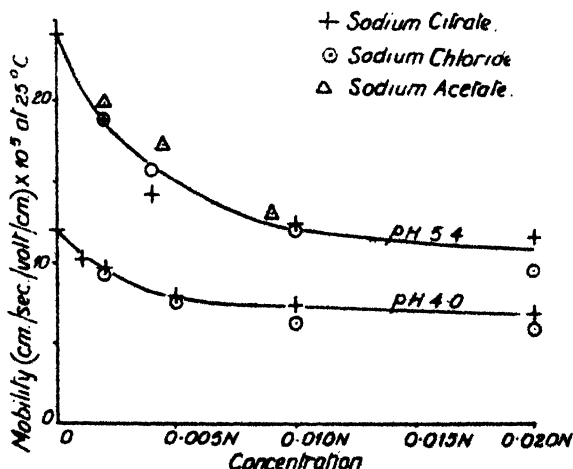


FIG. 5.—The effect of Sodium salts on the mobility of Tristearin.

chloride, citrate and acetate. The mobility is also shown at p_H 4 for sodium chloride and citrate as well as for the potassium salts previously employed (Fig. 6). The p_H value of 4 was chosen for the majority of

maintain the p_H values constant at all concentrations of the salts for, clearly, if a salt of a weak acid be added to an emulsion at p_H 5.6, the p_H value of the emulsion will be displaced to a more alkaline value and, since in this region the mobility is very sensitive to p_H change, erroneous effects will be observed unless precautions are taken to keep the p_H constant.

In Fig. 5 the mobility is given at p_H 5.4 approximately for different concentrations of sodium

⁶ Lachs and Biczysk, *Z. physik. Chem.*, 1930, 148, 441; Briggs, *J. Physic. Chem.*, 1928, 32, 1646; Tuorila, *loc. cit.*⁶

the concentration curves because, while the mobility is still reasonably large, the hydroxyl ion concentration, which seems to be an important factor in the determination of the charge, is sufficiently reduced to provide a fair opportunity for the primary adsorption of other ions.

In addition to the potassium chloride, phosphate and phthalate curves a curve has been obtained for various concentrations of potassium ferrocyanide, and for barium chloride.

For the measurements carried out at p_H 5.4 the p_H value was attained by the introduction of small amounts of very dilute hydrochloric acid in the case of the sodium chloride. For the sodium citrate it was found sufficient to dilute the stock solution of secondary sodium citrate with water or emulsion as required. The sodium acetate used was a mixture of nine parts of $N/10$ sodium acetate and one part of $N/10$ acetic acid, suitably diluted.

At p_H 4 the p_H is readily attained for sodium chloride, and for potassium chloride, phosphate and phthalate, and also for barium chloride, a slight adjustment being made with dilute hydrochloric acid. The sodium citrate was a mixture of $N/10$ secondary sodium citrate and $N/10$ hydrochloric acid containing 57 ml. of the salt solution to 43 ml. of acid solution and having a p_H of 4. This was then diluted as necessary, additional quantities of acid being added at the higher dilutions. For the ferrocyanide measurements also it was necessary to add one part of $N/10$ hydrochloric acid to 10 of $N/10$ potassium ferrocyanide solution and dilute to the required strength.

The experimental data are given in Figs. 5 and 6. If the fact that the mobility is sensitive

to small p_H changes at p_H 5.4 be borne in mind, it may be concluded that at this p_H the anions exhibit only minor specific effects and that the concentration curve is substantially the same in the three cases. At p_H 4, however, the sensitivity of the mobility to p_H is not so marked and the difference observed in the mobilities of sodium chloride and citrate respectively must be taken as a real though small effect. Similarly in the case of the potassium salts examined all, except phthalate, give the same curve. It is interesting to note that, when the p_H is kept constant, the results for the mobilities in ferrocyanide solutions are identical with those for the chloride solutions. Large specific effects have frequently been assumed for this ion and, in some cases at least, it seems likely that the p_H alteration has been overlooked. It must not be assumed, however, that the substantial identity in the mobilities of potassium chloride and potassium ferrocyanide infers an identity of charge also, for the thickness of the diffuse double layer is by no means the same for both.

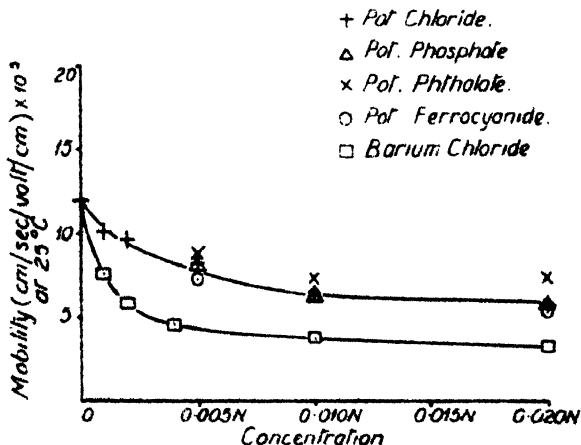


FIG. 6.—The effect of Potassium salts on the mobility of Tristearin at p_H 4 and a comparison with that of Barium Chloride.

(d) The Mobility of Tristearin Dispersions in the Presence of the Chlorides of the Alkali Metals.

In the previous sections it has been found that, other things being equal,

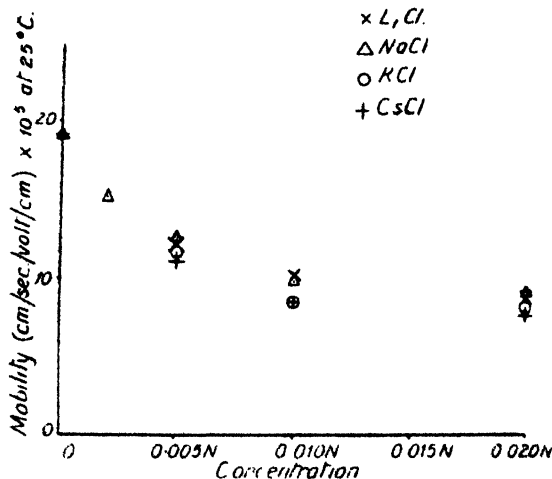


FIG. 7.—The effect of the alkali metal Chlorides on the mobility of Tristearin at p_H 5.0.

the different cations. Clearly, however, the caesium ion lowers the mobility more than the lithium ion.

(e) The Mobility of Dispersions of Tristearin in the Absence of Added Salts or Buffers.

As the previous results have shown, there is an appreciable lowering of the mobility of the fat in the presence of added salts as compared with the mobility of salt-free emulsions. Here a brief record is given of the data obtained when all electrolyte is eliminated except the small amount of acid, or for the highest p_H values, of alkali, necessary to obtain the appropriate p_H values. In the absence of other electrolytes, however, it becomes essential to investigate the effect of carbon dioxide, or more particularly, of the bicarbonate ion, in the emulsions. It has been found that many "inert" surfaces increase their charge on allowing the solutions to come into equilibrium with the carbon dioxide of the atmosphere. (cf. Abramson.)⁶

A preliminary investigation of the effect of dissolved carbon dioxide was carried out in the presence of citrate buffer, but no alteration in mobility could be detected between emulsions which were carbon dioxide-free and those which had been exposed to the atmosphere. Continuing the examination more closely, the buffer, which might mask or prevent any effect, was dispensed with. The carbon dioxide-free emulsions were made from freshly distilled boiling water, and immediately after adding the tristearin the flask was tightly stoppered and allowed to cool whilst a stream of washed carbon dioxide-free air was drawn through. For the supernatant liquid employed in the U-tube boiling distilled water was aspirated in the same manner. Mobility measurements were made on the emulsions between p_H 6.9 and 2 allowing them to make contact with the atmosphere for the shortest time possible. The mobility- p_H curve was plotted, the different p_H values being obtained by adding suitable

the potassium ion exerts a greater depressing effect upon the mobility than the sodium ion. The determinations are here extended by the examination of the mobilities in the presence of lithium and caesium chlorides, the p_H selected being p_H 5.0.

From the values shown in Fig. 7 it is evident that the lyotropic series is being observed, although the accuracy of the determinations is not sufficiently great to enable any quantitative relationship to be obtained between the effects of

⁶ Abramson, *Electrokinetic Phenomena*, p. 133.

amounts of dilute hydrochloric acid, or above p_H 6 of dilute caustic soda. The points were quite reproducible for three separate emulsions.

The above procedure was then repeated, except that in this case the air drawn through had not been freed of its carbon dioxide. The points fall closely upon the first curve and illustrate that under these conditions the effect of the bicarbonate ion is negligible.

Finally, an emulsion was prepared by adding the alcoholic solution to boiling, originally faintly alkaline, water, through which a rapid stream of washed carbon dioxide was being passed. This insured the presence of a fair concentration of bicarbonate ion in the water at the time of formation of the dispersion. The current of gas was continued until the whole attained room temperature. The p_H was varied as before by adding acid or alkali, but in this case the initial p_H of the stock emulsion was about 4.3. There was also a considerable amount of carbon dioxide in the dissolved gas state. Thus, on the introduction of caustic soda, relatively large amounts were necessary to obtain a reasonable p_H change on account of the buffering action of the carbonic acid present and the sodium bicarbonate formed. The mobilities are, therefore, somewhat depressed at the higher p_H values due to the effect of the increasing cation concentration. The experimental values are illustrated in Fig. 8. At lower p_H values the mobility for the carbon dioxide saturated emulsion is higher than that of the carbon dioxide-free emulsion. This effect is small and is not important. Fig. 8 also shows that the mobility curve in the "absence" of electrolyte lies above the corresponding curve in which there is a constant concentration ($N/100$) of sodium chloride.

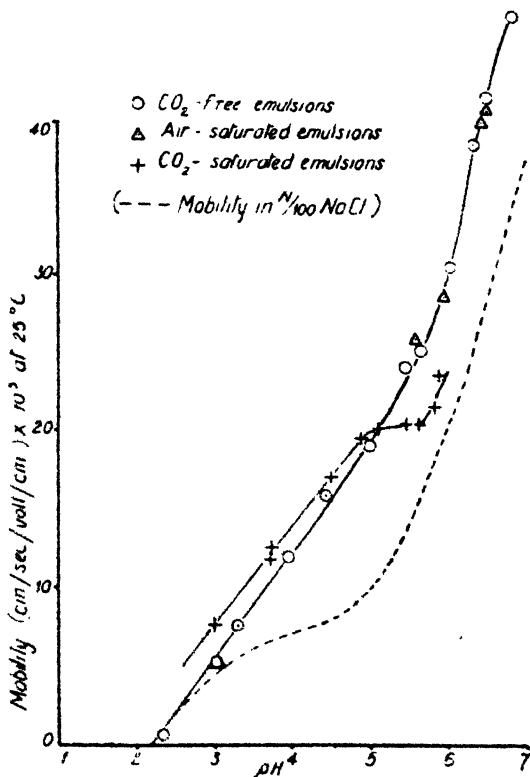


FIG. 8.—The mobility of Tristearin in electrolyte-free emulsions.

Discussion.

The general conclusion to be drawn from a consideration of the foregoing experiments is that the mobility is affected by added salts but that there is relatively little specific difference between the effects of salts containing cations of the same valency. As far as the electrophoretic mobility of the fat is concerned the effect of p_H on it stands out as the main controlling factor.

The mobility, however, is a function of the electrokinetic charge density and it would seem on general grounds that the latter should be regarded as the more fundamental property of the system. When the experimental facts are regarded from the point of view of the charge density they assume quite a different significance, but it is first necessary to consider the relationship between the two quantities, electrokinetic charge density and electrophoretic mobility.

The electrokinetic charge density is, of course, equal in magnitude and of opposite sign to the charge in the diffuse double layer, and the latter was first systematically treated by Gouy.⁷ He obtained an expression which gives a connection between the electrokinetic charge and the ζ -potential. The treatment is summarised by Müller⁸ and for a uni-univalent electrolyte and a flat double layer the expression reduces to

$$\sigma = 2\alpha \sqrt{c} \sinh \zeta/2\beta$$

where σ is the electrokinetic charge density,

ζ is the electrokinetic potential,

c is the concentration of electrolyte,

and α and β are constants.

In order to relate σ and u , the mobility, using the above equation it is necessary to connect ζ and u . The Smoluchowski relation

$$\zeta = \frac{4\pi\eta u}{D}$$

where η is the viscosity, u , the mobility under unit potential grad., and D the dielectric constant, is usually employed. This expression, however, is open to criticism and the connection between ζ and u has been redetermined more rigorously by D. C. Henry.⁹ Combined with the simple equation for the capacity of a concentric sphere condenser Henry gives the relationship between u and σ as

$$\sigma = \frac{u\eta (1 + \kappa a)}{a} \cdot \frac{1}{f(\kappa a)}$$

in which $f(\kappa a)$ is a quantity depending upon κ , the reciprocal of the "thickness" of the diffuse double layer, and a is the radius of the particle. This equation is more satisfactory than the Gouy expression for the lower values of ζ , or u , and when κa is less than 300. Above the latter value the two expressions are the same but at higher potentials the equations of the electric field which are used by Henry begin to fail.

In the case of the tristearin dispersions it is legitimate to employ the usual value of the mean radius of the particles for dilute emulsions of this nature, namely about 5×10^{-5} cm. and the correction, $f(\kappa a)$, is only of importance for the salt-free emulsions.

Calculation shows that, in the absence of salt, the σ increases with decrease in p_H ; when salt is present, however, σ rises very rapidly indeed either with increasing salt concentration at fixed p_H value or with increasing p_H at fixed salt concentration. With respect to the variation in charge density with p_H the values of σ have been calculated

⁷ Gouy, *J. Physique*, 1910, 9, 457.

⁸ Müller, *Cold Spring Harbor Symposium of Quantitative Biology*, p. 1 (1933).

⁹ Henry, *Proc. Roy. Soc., A*, 1931, 133, 124.

at different p_H values in the presence of different concentrations of sodium chloride and also for the salt-free case. Inspection of Table II. shows that σ is 61 e.s.u. at p_H 6 and 82 e.s.u. at p_H 5 in the absence of any sodium chloride. In $N/100$ sodium chloride at p_H 6 σ is 1790 e.s.u. and falls to 870 e.s.u. at p_H 5. Now if the primary charge were due solely to the anions present, i.e. hydroxyl and chloride, and if further the secondary layer were entirely diffuse, as postulated by Gouy, this fall must be due to removal of the hydroxyl ion from the surface, the chloride ion charge (if any) probably remaining constant. The

TABLE II.—THE ELECTROKINETIC CHARGE DENSITY σ IN e.s.u. CALCULATED FROM THE OBSERVED MOBILITIES IN SODIUM CHLORIDE SOLUTIONS USING THE HENRY EXPRESSION.

p_H	Charge Density.			
	Conc. of NaCl.			
	Nil.	0.002N.	0.005N.	0.010N.
7.0	—	2250	2640	3160
6.0	61	1090	1480	1790
5.0	82	600	770	870
4.0	125	420	490	630
3.0	160	250	350	440
2.2	0	0	0	0

loss, however, is far greater than the total charge density due to the hydroxyl ion, as calculated from the salt-free case.* It follows, therefore, that the total density of charge on the primary layer must be considerably greater than the value of σ calculated but that at the same time a proportion of the cations present have effectively annulled a corresponding part of this charge density. This is in agreement with the concept of Stern¹⁰ in which a secondary rigid layer is postulated as well as a diffuse layer. Then in the case of the dispersions containing a constant salt concentration the fall in electrophoretic charge density with decrease in p_H may be explained assuming that hydrogen ions enter the secondary rigid layer or that the primary charge density decreases due to loss of hydroxyl ion. It is to be expected that the amount of hydrogen ion so adsorbed will be a function of the initial magnitude of the effective primary charge, and inspection of the charge density table shows that the fractional fall in σ with fall on p_H at the different salt concentrations is indeed approximately the same in each case. Attempts, however, to fit the experimental values to a simple Langmuir adsorption equation, of the type predicted by the law of mass action, fail.†

Turning to the case of increasing salt concentration whilst maintain-

¹⁰ Stern, *Z. Elektrochem.*, 1924, 30, 508.

* Although in this case the charge density is increasing with decrease in p_H , a maximum must be passed through as eventually, at p_H 2.2 the mobility, and therefore the electro-kinetic charge density, falls to zero. Further, in the presence of NaCl the mobility was likewise found to reach zero value at the same p_H , viz., 2.2, indicating that the "discharging" efficiency of hydrogen ion is far greater than that of the alkali metal ion.

† It seems reasonable to assume that the amount of a cation rigidly adsorbed in the secondary layer, besides being a function of the bulk concentration of that ion, would be affected by the magnitude of the primary charge. Thus, on increasing the primary charge, by raising the concentration of the sodium chloride, it is to be expected that, even though the hydrogen ion concentration were maintained at a constant value in the bulk, the amount of this ion rigidly adsorbed would increase. Such an increase would account for the failure of the simple adsorption equation.

ing a constant p_H value, here the concentrations of the two added ions, sodium and chloride, are increasing at the same rate, but also, probably the amount of hydrogen ion adsorbed will be governed by the increase in the concentration of the sodium chloride.

In addition to the data just discussed, in which we are concerned chiefly with the effect of altering the p_H in the presence of a single

TABLE III.—THE EFFECT OF VARIOUS SALTS UPON σ AT FIXED p_H .

Charge Density (in e.s.u.).

Concn. N.	NaCl or LiCl.	KCl.	CsCl.
A. Results Obtained at $p_H = 5$.			
0.005	770	730	690
0.01	870	770	740
0.02	1130	1000	940

Concn. N.	NaCl.	KCl.	$K_4Fe(CN)_6$.	$BaCl_2$.
B. Results Obtained at $p_H = 4$.				
0.005	490	490	770	350
0.01	630	570	980	410
0.02	840	690	1310	510

cases there is a decrease in *mobility* with increasing salt content, particularly so in the case of $BaCl_2$). Table III. A shows that the lightly hydrated caesium ion finds its way more readily into the rigid part of the secondary layer than does the heavily hydrated lithium or sodium ion. In Table III. B the case of $K_4Fe(CN)_6$ is of special importance as showing either a primary adsorbability of the multivalent anion, or an enhanced removal of H^+ ion by union with the ferro-cyanide anion. The charge density in this case is appreciably greater than that for KCl although the mobilities in these two cases are indistinguishable. The κ term is of course greater in the case of the ferro-cyanide.

Summary.

(1) The electrophoretic mobility of purified tristearin in different buffer solutions has been examined as a function of p_H between the p_H values 2 and 7. The variation of the mobility with p_H in sodium and potassium chloride solutions has likewise been measured.

(2) The effects of different added anions has been found at fixed p_H values. The mobility is found to be chiefly a function of the salt concentrations rather than of the individual ions.

(3) The mobility has been observed in the alkali metal chloride solutions at constant p_H . The lyotropic series appears to hold but the differences are slight.

(4) The variation of mobility with p_H in the absence of any electrolyte, except that necessary to attain the p_H values has been determined. The effect of small amounts of dissolved CO_2 is found to be negligible.

typical uni-univalent salt, NaCl, the mobility data shown in the graphs likewise permit of a comparison of various salts at a fixed p_H . The resulting charge densities are summarised in Table III. (The effects produced by NaCl and LiCl are indistinguishable.)

Considering the results of both sections of the above table it will be seen that in all cases there is an increase in σ with increase in salt concentration, even in the case of barium chloride, although in the latter case as might be expected the influence of the barium ion acts as a depressing agent. (It will be recalled that in all

(5) In connection with the relation between the electro-kinetic charge density σ and the mobility, calculation shows that σ increases with fall in p_H in the "absence" of electrolyte, but decreases with fall in p_H if salt is present. Further, σ is found to increase with rising salt concentration at constant p_H .

(6) In order to account for the variation in σ it is necessary to assume either primary adsorption of the added anions, or exchange of H^+ ion in the rigid secondary layer by the added cations, producing a less tightly bound system, thus increasing the effective electrokinetic charge. Under comparable conditions as regards concentration, H^+ ion is much more strongly adsorbed into the rigid secondary layer than is any other cation. Exchange, in the sense of removal of H^+ ion, is only brought about when the concentration of the added cation is much greater than that of H^+ ion.

(7) It is concluded that the amount of hydrogen ion adsorbed in the rigid secondary layer is a function of the effective primary charge as well as of p_H .

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THE EFFECT OF DILUTE HYDROCHLORIC ACID ON THE SURFACE TENSIONS OF AQUEOUS SALT SOLUTIONS.

BY J. W. BELTON.

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The calculation of the adsorption of the components at the surface of a ternary solution involves a knowledge of the change in surface tension with the concentration of each solute, and of the variation of the activity coefficients of the components with the composition of the solution. These data are frequently difficult to obtain, but in the case of certain solutions, such as those containing hydrochloric acid and salts, simplifications may be made and the surface adsorptions calculated.¹

It has been shown previously² that the presence of 0.1 *M* hydrochloric acid produces a measurable change in the surface tensions of aqueous solutions of sodium and potassium chlorides, the effect increasing with increasing salt concentration. These measurements have now been extended to solutions containing other salts and the surface adsorptions calculated. The surface tension of the acid solution alone is only 0.02 dyne/cm. less than that of pure water, an amount of the order of the experimental error; it might be therefore expected that the presence of dilute acid in strong salt solutions could be neglected. The effect of the two solutes on the surface tension is, however, not equal to the sum of the effects produced by each when present separately.

Experimental.

The surface tensions were measured by the bubble pressure method previously described,³ and were calculated from the expression

$$\gamma = \frac{rg}{2} \left(h\rho - \frac{2}{3}r\rho \right) \quad \dots \quad (1)$$

where r is the radius of the jet, g is 981.2 cms./sec.², h is the maximum bubble pressure in cms. of butyl phthalate, the manometric liquid, ρ is

¹ Belton, *Trans. Faraday Soc.*, 1935, 31, 1413.

² *Ibid.*, 1648.

the density of butyl phthalate at 25° (1.0434 gms./c.c.), and ρ_1 the density of the solution under examination. Two jets were used in this investigation, one of radius 0.0102 cm., the other 0.0104 cm.; both were broken

TABLE I.

Salt.	m.	h.	γ .	$\Delta\gamma$.	h_1 .*
(a) Surface Tensions of Aqueous Salt Solutions.					
LiCl	1.36	13.915	74.23	2.22	1.63
	1.88	14.08	75.10	3.09	1.64
	2.67	14.31	76.30	4.29	1.59
	3.67	14.64	78.10	6.09	1.66
CaCl ₂	0.37	13.71	73.13	1.12	3.02
	0.74	13.93	74.30	2.29	3.09
	1.11	14.15	75.48	3.47	3.13
	1.48	14.365	76.67	4.66	3.14
SrCl ₂	0.48	13.79	73.55	1.54	3.21
	0.96	14.065	75.02	3.01	3.14
	1.44	14.375	76.68	4.67	3.25
	1.92	14.75	78.68	6.67	3.47
BaCl ₂	0.49	13.78	73.50	1.49	2.90
	0.965	14.05	74.93	2.92	2.89
	1.42	14.32	76.38	4.37	3.07
NaClO ₄	0.52	13.565	72.36	0.35	0.67
	1.03	13.62	72.65	0.64	0.62
	1.54	13.66	72.86	0.85	0.55
Na ₂ S ₂ O ₈	0.49	13.76	73.40	1.39	2.84
(b) Surface Tensions of 0.1 M Hydrochloric Acid—Salt Solutions.					
LiCl	0.55	13.67	72.92	0.90	1.64
	1.89	14.04	74.88	2.87	1.52
	2.88	14.395	76.78	4.77	1.65
	3.91	14.63	78.05	6.04	1.54
	4.88	14.94	79.70	7.69	1.57
CaCl ₂	0.37	14.025	73.20	1.19	3.21
	0.74	14.215	74.21	2.20	2.96
	1.11	14.40	75.17	3.16	2.86
	1.48	14.595	76.21	4.20	2.83
SrCl ₂	0.48	14.10	73.60	1.59	3.31
	0.96	14.45	74.81	2.80	2.92
	1.44	14.305	76.32	4.30	2.98
	1.92	14.615	77.98	5.97	3.10
BaCl ₂	0.45	13.74	73.30	1.29	2.87
	0.82	13.91	74.20	2.19	2.67
	1.13	14.095	75.18	3.17	2.80
NaClO ₄	0.50	13.53	72.16	0.15	0.30
	0.96	13.565	72.36	0.35	0.36
	1.34	13.595	72.51	0.50	0.37
Na ₂ S ₂ O ₈	0.455	13.73	73.23	1.22	2.68

* Last column in b refers to h_1' and not h_1 .

clean and were circular in cross-section. The surface tensions of pure water and of pure benzene found with both jets agreed with the standard values. Solutions were made up by weight in stoppered flasks from Analar salts, some of which had been further treated for the removal of water, and from a stock solution of 0.1 *M* hydrochloric acid. In the case of barium chloride, sodium perchlorate and sodium dithionate the hydrated salt was used and the solution made 0.1 *M* with respect to hydrochloric acid by the addition of a calculated weight of acid of strength greater than 0.1 *M*. For purposes of comparison, parallel measurements were made on salt solutions not containing acid. All measurements were made at 25.°

The results obtained are given in Table I. (a) and (b) which refer to salt solutions and to salt-acid solutions respectively. Each part of the Table gives the salt present, its concentration, *m*, in moles per 1000 gms. of water, the manometric reading, the surface tension (γ), the surface tension increment, $\Delta\gamma$, ($\gamma_0 = 72.01$ dynes/cm.), and the value of *k* calculated from it.

In each case the presence of the acid reduces the surface tension, the effect increasing with increasing salt concentration. The surface tensions of the salt solutions are given by the relation

$$\gamma - \gamma_0 = k_1 m_1$$

where k_1 is a constant, while those of the acid-salt mixtures are given by a similar relation in which the constant (k_1') is less than k_1 .

Application of the Gibbs Equation.

In the salt solutions water is positively adsorbed at the surface, while in hydrochloric acid solutions, for which the surface tension decreases with increasing acid concentration, the acid is positively adsorbed. In solutions containing both components we may expect both water and acid to be positively adsorbed. According to the Gibbs equation

$$d\gamma = -\Gamma_1 d\mu_1 - \Gamma_2 d\mu_2 - \Gamma_3 d\mu_3 \quad (2)$$

in which Γ_1 , Γ_2 and Γ_3 are the surface adsorptions of salt, acid and water respectively, and μ_1 , μ_2 and μ_3 are their chemical potentials. If the dividing surface is drawn so that the concentration of salt is zero, this becomes

$$d\gamma = -\Gamma_2 d\mu_2 - \Gamma_3 d\mu_3 \quad (3)$$

A relation between the mole fractions (*n*) of the components and their chemical potentials is given by the Duhem-Margules equation, according to which

$$n_1 d\mu_1 + n_2 d\mu_2 + n_3 d\mu_3 = 0 \quad (4)$$

Substituting for $-d\mu_3$ in (3) we obtain

$$d\gamma = -\Gamma_2 d\mu_2 + \Gamma_3 \left(\frac{n_1}{n_3} d\mu_1 + \frac{n_2}{n_3} d\mu_2 \right) \quad (5)$$

$$= -\Gamma_2 2RT \, d \log f_2 m_2 + \Gamma_3 \frac{m_1}{55.55} 2RT \, d \log f_1 m_1 + \Gamma_3 \frac{m_2}{55.55} 2RT \, d \log f_2 m_2 \quad (6)$$

where *f* is the appropriate activity coefficient. If the acid concentration is kept constant and that of the salt varied

$$\left(\frac{d\gamma}{dm_1} \right)_{m_2} = -\Gamma_2 2RT \left(\frac{\partial \log f_2}{\partial m_1} \right)_{m_2} + \Gamma_3 \frac{m_1}{55.55} 2RT \left(\frac{1}{m_1} + \left(\frac{\partial \log f_1}{\partial m_1} \right)_{m_2} \right) + \Gamma_3 \frac{m_2}{55.55} 2RT \left(\frac{\partial \log f_2}{\partial m_1} \right)_{m_2} \quad (7)$$

The acid adsorption, Γ_2 , is much smaller than Γ_1 (of the order 10^{-12}), and consequently the first term on the right-hand side may be neglected and (7) becomes

$$\left(\frac{\partial \gamma}{\partial m_1}\right)_{m_2} = \frac{\Gamma_1 2RT}{55.55} \left(1 + m_1 \left(\frac{\partial \log f_1}{\partial m_1}\right)_{m_2} + m_2 \left(\frac{\partial \log f_2}{\partial m_1}\right)_{m_2}\right). \quad (8)$$

The surface concentration of water for a solution without acid is given by the Gibbs equation applied to a system of two components

$$d\gamma = - {}_0\Gamma_3 d\mu_3$$

or
$$\frac{d\gamma}{dm} = - {}_0\Gamma_3 \frac{m_1}{55.55} 2RT \left(\frac{1}{m_1} + \frac{d \log f_1}{dm}\right) \quad (9)$$

Further $d\gamma/dm = k_1$ the experimentally determined constant. If the effect of 0.1 *M* hydrochloric acid on the $\partial \log f/\partial m$ term is neglected, and (8) and (9) are combined, we obtain

$$\left(\frac{\partial \gamma}{\partial m_1}\right)_{m_2} = \Gamma_3 \left[-\frac{k_1}{{}_0\Gamma_3} + \frac{m_2}{55.55} 2RT \left(\frac{\partial \log f_2}{\partial m_1}\right)_{m_2}\right] \quad (10)$$

from which values of Γ_3 may be computed. Values of ${}_0\Gamma_3$ may be obtained directly from the vapour pressure (*p*) of water over the solutions

$${}_0\Gamma_3 = -\frac{d\gamma}{d\mu_3} = -\frac{d\gamma}{RT d \log p} = -\frac{p}{RT} \frac{d\gamma}{dp} \quad (11)$$

Hence

$$\Gamma_3 = k_1' \left/ \left[k_1 \frac{RT}{p} \cdot \frac{\Delta p}{\Delta \gamma} + \frac{m_2}{55.55} 2RT \left(\frac{\partial \log f_2}{\partial m_1}\right)_{m_2} \right] \right. \quad (12)$$

The values of Γ_3 in moles/sq. cm. calculated in this way are given in Table II. The experimental data for sodium and potassium chloride solutions have been taken from the previous paper.³ The vapour pressures of water for solutions of sodium, potassium and lithium chlorides have been taken from the measurements of Pease and Nelson,³ and for solutions of calcium, strontium and barium chlorides from the data of Hepburn.⁴ The values of $(\partial \log f_2/\partial m_1)_{m_2}$ have been calculated

TABLE II.

Salt.	NaCl.		KCl.		LiCl.		CaCl ₂ .		SrCl ₂ .		BaCl ₂ .	
<i>m</i> ₁ .	<i>Γ</i> ₂ .	<i>Γ</i> ₃ .	<i>Γ</i> ₂ .	<i>Γ</i> ₃ .	<i>Γ</i> ₂ .	<i>Γ</i> ₃ .	<i>Γ</i> ₂ .	<i>Γ</i> ₃ .	<i>Γ</i> ₂ .	<i>Γ</i> ₃ .	<i>Γ</i> ₂ .	<i>Γ</i> ₃ .
0.5	21.4	20.0	21.5	20.2	20.6	19.0	20.0	18.0	24.4	21.0	31.3	30.2
1.0	20.0	18.5	21.7	20.6	17.3	15.8	12.3	11.5	18.0	16.2	22.9	22.0
1.5	18.6	17.2	20.6	19.6	14.6	13.4	9.3	8.9	15.0	13.8	17.2	16.6
2.0	17.5	16.1	19.5	18.4	12.6	11.8	7.6	7.3	12.9	11.8	13.0	12.6
2.5	16.3	15.0	18.6	17.3	11.3	10.8	6.5	6.2	11.0	10.1	—	—
3.0	15.0	13.8	17.5	16.2	10.2	9.8	5.6	5.3	9.5	8.7	—	—
3.5	13.8	12.8	16.6	15.0	9.3	8.9	4.9	4.7	—	—	—	—
4.0	13.0	12.0	—	—	8.6	8.0	—	—	—	—	—	—
4.5	12.4	11.5	—	—	7.8	7.3	—	—	—	—	—	—
5.5	—	—	—	—	6.7	6.2	—	—	—	—	—	—

³ Pease and Nelson, *J. Amer. Chem. Soc.*, 1932, 54, 3544.

⁴ Hepburn, *J. Chem. Soc.*, 1932, 550.

from the data of Harned⁶ for the above solutions; for sodium perchlorate-acid solutions the data of Bates and Urmston⁶ were employed, and for sodium dithionate-acid solutions that of Murdoch and Barton.⁷ In all cases it was found that the value of $(\partial \log f_2 / \partial m_1)_{m_2}$ was small, and that the second term on the right-hand side of (10) may be neglected with only a small error. In one case, for example the first term was of the order 0.1×10^{10} , while the second was 0.001×10^{10} . The values of $(\partial \log f_2 / \partial m_1)_{m_2}$ have, therefore, not been tabulated. The surface concentrations given in the table are smoothed values obtained by plotting the calculated values against the salt concentration; they are given in moles/sq.cm. $\times 10^{10}$.

In all cases the amount of water adsorbed is reduced by the presence of acid, and by an increase in the concentration of the last. The thickness of the adsorbed layer in Å. may be obtained by multiplying the tabulated values of Γ_2 by the molecular weight of water. The area occupied per molecule in the layer, assuming it to be unimolecular, is given by $1/\Gamma_2 N$.

Table III. gives the ratio of the area per molecule of water in the surface of solutions containing salt of concentration $3M$ (A_0) to that for salt solutions of the same concentration containing acid (A_s). The values of Γ_2 for sodium perchlorate and for sodium dithionate solutions have not been calculated because of the lack of reliable vapour pressure data, but the value of A_0/A_s is given. These figures also give the factor by which the thickness of the adsorbed water layer is reduced by the addition of acid. Table III. also gives the area in Å² occupied per molecule of water in the surface for a number of acid-salt mixtures of salt concentration $3M$. The area occupied per molecule of water corresponding to an adsorption of 20×10^{-10} moles/sq. cm., which is the value found for some of the more dilute solutions, is 8.25 Å^2 ; the area of cross-section of a water molecule is of the order 7 Å^2 , and the adsorption corresponding to this area, that is to a saturated unimolecular layer, is 23×10^{-10} moles/sq. cm.

TABLE III.

Salt.	NaCl	KCl	LiCl	CaCl ₂	SrCl ₂	BaCl ₂	NaClO ₄	Na ₂ S ₂ O ₆
A_0/A_s	0.92	0.87	0.96	0.95	0.92	0.96	0.60	0.94
A_s	12	11	16	32	19	—	—	—

Summary.

The surface tensions of aqueous solutions of lithium chloride, calcium chloride, strontium chloride, barium chloride, sodium perchlorate and sodium dithionate, and of ternary solutions of these salts and $0.1M$ hydrochloric acid have been measured by the maximum bubble pressure method. The presence of the acid produces a lowering of the surface tension, the effect increasing with increasing salt concentration. The amount of water adsorbed at the surface of the ternary solutions has been calculated from the Gibbs equation.

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⁶ Harned, *J. Amer. Chem. Soc.*, 1922, 44, 2729.

⁶ Bates and Urmston, *ibid.*, 1933, 55, 4068.

⁷ Murdoch and Barton, *ibid.*, 4074.

THE ELECTRODEPOSITION OF SHEET CHROMIUM.

BY R. H. ROBERTS.

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In connection with some work on the electrolytic passivation of metals, the need arose for some plates of pure chromium of sufficient thickness to permit of prolonged dissolution of the metal. Adcock¹ has succeeded in preparing large quantities of the metal in a high degree of purity; his product however was apparently in the form of irregular fragments which would require melting in a controlled atmosphere before they could be reduced to a form suitable for electrodes. He describes a high frequency induction furnace which served admirably for this purpose, but since such apparatus was not available in this laboratory an attempt had to be made to prepare thick, coherent layers of metal by direct electrodeposition.

A search of the literature for the most suitable composition of plating bath revealed that whilst there is general agreement regarding the optimum concentration of chromic anhydride, opinions differ widely as regards temperature, current density, and the quantity and nature of additional electrolytes, among which sulphuric acid, chromic sulphate, sodium sulphate and even acetic acid have received attention. Preliminary experiments seemed only to support this uncertainty since variation in concentration of sulphate or, within reason, of sulphuric acid had very little effect on the nature of the deposit. The temperature, however, should not be below 40° or above 50° C.

Where, as here, the primary requirement is thickness of deposit with uniformity of surface, the shape of the cathode has been found to be of fundamental importance. It was soon evident that any cathode approaching the form of a flat plate was quite impracticable, as nearly all the chromium was deposited as nodular excrescences at the edges and, in particular, at the corners of the cathode; even the amount of inequality of curvature involved in a cathode of elliptical section (*e.g.* a partially flattened tube) was found to be sufficient to cause preferential deposition, generally of an irregular nature, on the areas of greatest curvature. This variability of thickness of deposit was emphasised at higher current densities. With the ideal shape of electrode high currents are to be avoided on account of the nodular growths encouraged under such conditions; on the other hand a limit is set to the minimum current which may be employed by a sharp fall in efficiency of deposition. A value of 12.5 amps. per dcm.² was found to be most satisfactory.

With these points in mind cathodes of brass and bronze were constructed to the form of hollow cylinders with the lower ends turned to hemispherical shape. One of these was arranged in the bath to rotate about a vertical axis. The outer surface, on which the chromium was to be deposited, was of course highly polished before immersion.

Further details are probably best illustrated by the following data referring to one typical run.

¹ Adcock, *J. Iron and Steel Inst.*, 1927, 118, 369.

Cathode : Brass cylinder 1.28 cm. diam. terminated by a hemisphere, immersed to a depth of 5.2 cm. (Area immersed 21 cm.²).

Speed of rotation : 60 r.p.m.

Anodes : Two lead sheets, 1.3 cm. wide, immersed, on opposite sides of cathode, to a depth of 4 cm.

Bath : 250 g. CrO₃ (pure), 3 g. Cr₂(SO₄)₃ (anhydrous), water to 1 litre.

Temperature : 42° C.

Current strength : 2.2 amp.

Time of electrolysis : 7 days (168 hours).

Weight of metal deposited : 16.025 g.

Thickness of deposit (by micrometer) : At top of cylinder, 1.04 mm., at bottom, 0.87 mm.

This represents an efficiency of deposition of 13.4 per cent. assuming six faradays per gram-atom of metal.

The surface of the chromium was uniformly of a bright "satin" type, except for a few (in this instance, ten) small nodules, none more than two millimetres in diameter, which had the appearance of having been produced by prolonged adherence of gas bubbles at those particular points.

It must be admitted that the time of deposition is long and the current efficiency not good ; for the purpose of the work in hand, however, these considerations were of minor importance.

To remove the metal from the cathode, slots were milled through the chromium by means of a high speed carborundum wheel and the basis metal was dissolved away in nitric acid. The curved plates so formed were hard and brittle ; they could, however, be softened by heating in hydrogen to 1600 or 1700° C. The hydrogen was subsequently removed by evacuation at 900°.

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REMARKS ON THE INCORPORATION OF THERMODYNAMIC VARIABLES IN CHEMICAL KINETICS.

By E. A. MOELWYN-HUGHES (*Messel Research Fellow of the Royal Society*).

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Arrhenius's conception of an energy of activation, the first point of contact between thermodynamics and chemical kinetics, is based on analogy between van't Hoff's expression for the temperature variation of a chemical equilibrium constant, namely,

$$\frac{d \ln K}{dT} = \frac{Q}{RT^2} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (1)$$

and Arrhenius's relation for the temperature variation of a velocity constant, namely,

$$\frac{d \ln k}{dT} = \frac{A}{RT^2} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (2)$$

Subsequent theoretical developments have been concerned with the nature of the equilibrium which, according to Arrhenius, exists between

passive and active molecules. Arrhenius himself, regarding A as independent of temperature, wrote

$$\ln k = \ln B - \frac{A}{RT} \quad (3)$$

The thermal change, Q , which accompanies a chemical reaction is, however, in general a function of temperature. Consistency with the kinetic relation

$$K = \frac{k_2}{k_1} \quad (4)$$

suggests the desirability of expressing A also as a function of temperature, and accounts for the many early attempts made in this direction.

Experimental Approaches to the Study of Intermediate Complexes.

When, as it is not infrequently found, the kinetic order of chemical change does not coincide with, but is lower than, the stoichiometric order, the observed velocity constant must be a composite quantity, involving either simultaneous or consecutive changes, so that the Arrhenius equation can no longer have the relatively simple meaning which it has for elementary processes. The idea of an intermediate complex, possessing chemical individuality in addition to the physical peculiarity postulated by Arrhenius, emerged from the attempt to reconcile chemical complications with kinetical simplicity. Attempts, which we shall now illustrate, to extricate a single rate-determining step have led to the idea of an intermediate complex in connection with two distinct sets of phenomena.¹ The potential reactants, A and B, are supposed not to undergo measurable chemical change directly but first to establish a state of equilibrium:—



The measurable rate is assumed to be that of the decomposition of the complex, AB,



hence
$$+ \frac{d[C]}{dt} = k_3[AB] = k_3K[A][B]$$

and since
$$k_{\text{obs.}} = \frac{1}{[A][B]} \cdot \frac{d[C]}{dt} \quad (7)$$

we have
$$k_{\text{obs.}} = k_3K \quad (8)$$

If C or D is identical with either A or B, the mechanism is catalytic. Michaelis (1913) applied this form of the intermediate-complex theory to the case where A is an enzyme and B is the substrate which it decomposes. Bjerrum and Brønsted (1923) independently applied the same principle to the case where A and B are both ions. Generally, K must be expressed in terms of activities rather than concentrations (G. N. Lewis, 1907; Debye and Hückel, 1922). Hence the K values of

¹ For a review, see Moelwyn-Hughes, *The Kinetics of Reactions in Solution*, p. 139, Oxford, 1933.

equations 5 and 8 must be multiplied by a factor f , which in this case is related to the separate activity coefficients by the equation

$$f = \frac{f_{AB}}{f_A f_B} \quad (9)$$

Combining with equation (8), we may write:—

$$\begin{aligned} (\text{Velocity at ordinary dilutions}) &= (\text{Velocity at infinite dilution}) \\ &\times \frac{f_{AB}}{f_A f_B} \quad (9a) \end{aligned}$$

Brönsted and Bjerrum differ in the choice of the rate-determining process, but the two views can be reconciled by adopting the stationary concentration hypothesis of Christiansen (1923). The expression for the concentration of the intermediate complex, assumed to have reached a stationary value, is

$$[AB]_{\text{stat.}} = \frac{k_2[A][B]}{k_1 + k_3} \quad (10)$$

Ex hypothesi the rate of reaction equals $k_3[AB]_{\text{stat.}}$ so that

$$k_{\text{obs.}} = \frac{k_2 k_3}{k_1 + k_3} \quad (11)$$

When $k_1 \gg k_3$, there results the Brönsted condition

$$k_{\text{obs.}} \cong k_2 \cdot \frac{k_3}{k_1} \cong k_3 K \quad (12)$$

When $k_1 \ll k_3$ there results the Bjerrum condition

$$k_{\text{obs.}} \cong k_3 \quad (13)$$

Empirical relations between velocity constants and equilibrium constants have also been discovered by Brönsted and Guggenheim, by Hammett (1928), and by Horiuti and Polanyi (1935). They signify a relation between energies of activation and heats of ionisation, and should prove helpful in ascribing energy levels to various intermediate complexes.

As the critical complex has only a transitory existence, our information concerning it is based on theoretical inference.

Theoretical Approaches to the Study of Intermediate Complexes.

Theoretical approaches to the investigation of reactive complexes have been of two kinds: (1) We may select any molecule or pair of like or dissimilar molecules, and, making *ad hoc* postulates concerning its structure, we may construct the dynamical expressions which serve to describe its properties, among which chemical decomposition is one. (2) We may place full faith on equation (4), using an accurate expression for K , in thermodynamic or, preferably, statistical form. Then, armed with a fairly complete knowledge of what k_2 means, we arrive at an expression for k_1 , from which the required information about the complex emerges.

(1) F. Krüger² considers the relative probability that a labile atom in a polyatomic molecule may be found inside or outside a "sphere of action," while A. March³ makes use of the idea that the complex may be dissociated or not, according as the generalised co-ordinates exceed

² *Gott. Nachr.*, 1908, 318.

³ *Physikal. Z.*, 1917, 18, 53.

or are less than a certain limiting value. Dissociation or recombination is represented by the passage of the representative point in opposite directions through a critical area in phase space. Similar ideas have been much further developed by Pelzer and Wigner.⁶ The simplest hypothetical picture of an active complex which has been presented is that of Goldschmidt,⁵ who regards it as a normal molecule possessing an excess of kinetic energy.

(2) Efforts to study the intermediate complex by the second method have been much more numerous. As an example, we shall consider the theory of K. F. Herzfeld.⁶ Using Stern's expression⁷ for the dissociation constant of diatomic molecules, namely,

$$K = \frac{[AB]}{[A][B]} = h d^3 \left\{ \frac{8\pi}{kT} \left(\frac{1}{m_A} + \frac{1}{m_B} \right) \right\}^{\frac{1}{2}} (1 - e^{-h\nu/kT})^{-1} e^{-Q/RT} \quad (14)$$

and Trautz's expression for the rate of combination of atoms, assuming zero energy of activation, namely,

$$k_2 = s^3 \left\{ \frac{8\pi kT}{m_A} + \frac{1}{m_B} \right\}^{\frac{1}{2}} \quad . \quad . \quad . \quad (15)$$

Herzfeld obtains, by means of equation (4), the following expression for the velocity of dissociation

$$k_1 = \frac{k_2}{K} = \frac{kT}{h} \cdot \left(\frac{s}{d} \right)^3 (1 - e^{-h\nu/kT}) e^{-Q/RT} \quad . \quad . \quad . \quad (16)$$

If we identify the collision diameter (d) with the equilibrium separation (s) of the atoms in the molecule, the "steric" factor disappears, giving us

$$k_1 = \frac{kT}{h} \cdot (1 - e^{-h\nu/kT}) e^{-Q/RT} \quad . \quad . \quad . \quad (17)$$

Two special cases are of interest. When $h\nu \ll kT$,

$$k_1 = \nu e^{-Q/RT}, \quad . \quad . \quad . \quad (18)$$

an equation which was arrived at on very different grounds by Rideal (1920), Dushman (1921) and McKeown (1923). When $h\nu \gg kT$, we have

$$k_1 = \frac{kT}{h} \cdot e^{-Q/RT}, \quad . \quad . \quad . \quad (19)$$

which is the simplified form in which Herzfeld applied his equation to numerical examples. Very similar considerations have been recently and independently advanced by Rodebush,⁸ and Eyring (*vide infra*).

Entropy of Activation.

The idea of an entropy of activation originates with van't Hoff, who, however, did not give it that name. Van't Hoff's treatment is as

⁴ *Z. physikal. Chem.*, B, 1932, 15, 445; cf. *Annual Reports of the Chemical Society*, p. 94, 1936.

⁵ *Physikal. Z.*, 1909, 10, 206.

⁷ *Ibid.*, 1913, 44, 497.

⁶ *Ann. Physik*, 1919, 59, 635.

⁸ *J. Chem. Physics*, 1933, 1, 440.

follows.⁹ Generally, we have $d \ln K/dt = Q/RT^2$, where Q is the heat of reaction. Since $K = k_2/k_1$,

$$\frac{d \ln k_2}{dT} - \frac{d \ln k_1}{dT} = \frac{Q}{RT^2} \quad (20)$$

Now Q is usually a function of temperature; from Hess's equation, we obtain

$$Q_T = Q_0 + (C_2 - C_1)T \quad (21)$$

provided $(C_2 - C_1)$ is independent of temperature. We then have

$$\frac{d \ln k_2}{dT} - \frac{d \ln k_1}{dT} = \frac{Q_0}{RT^2} + \frac{(C_2 - C_1)}{RT} \quad (22)$$

Neither the empirical validity of the Arrhenius equation

$$d \ln k/dT = A/RT^2,$$

nor that of the van't Hoff equation $d \ln k/dT = A'/RT^2 + B$ permits of a resolution of the more complicated equation. Subsequent developments have, however, resulted from the dexterous splitting up of equation (22) into two equations alleged to account separately for the two velocity constants. The resolution is intuitive, and may or may not be justified by its consequences. Let it be assumed that we can write $Q_0 = Q_2 - Q_1$, and that we can also write

$$\frac{d \ln k_2}{dT} = \frac{Q_2}{RT^2} + \frac{C_2}{RT} \quad (23)$$

and

$$\frac{d \ln k_1}{dT} = \frac{Q_1}{RT^2} + \frac{C_1}{RT} \quad (24)$$

Provided the heats of activation and the specific heats of reactants and products are independent of temperature, we can integrate, writing

$$\ln k_2 = \text{constant} + \frac{C_2}{R} \ln T - \frac{Q_2}{RT} \quad (25)$$

and

$$\ln k_1 = \text{constant} + \frac{C_1}{R} \ln T - \frac{Q_1}{RT} \quad (26)$$

Generally, however, neither of these assumptions is valid, so that the expressions for the separate velocity coefficients contain terms of the form $\int \frac{dT}{T^2} C dT$. It is in this form that the analogue of thermodynamic entropy appears in kinetic studies.¹⁰

Within recent years, Soper has drawn attention to the possibility of interpreting deviations from normal behaviour of bimolecular reaction in solution in terms of entropy changes. By normal reactions we mean those for which P in the expression $k = ZPe^{-E_A/RT}$ has the order of magnitude unity; Z is the gas kinetic collision frequency. It is pointed out that the thermodynamic change in free energy accompanying a certain reaction in a series of solvents varies in the same direction as the observed Arrhenius A values for one of the reactions.¹¹ The possible

⁹ *Vorlesungen über theoretische und physikalische Chemie*, Vol. I., p. 228, Braunschweig, 1901.

¹⁰ Kohnstamm and Scheffer, *Verlag Akad. Wetensch. Amsterdam*, 1911, 19, 878; Trautz, *Z. physikal. Chem.*, 1910, 68, 637; *Z. Elektrochem.*, 1915, 25, 4.

¹¹ *Discussion on the Critical Increment*, p. 45, 1931; Chemical Society.

temperature variation of P , which must be roughly the same as that of the Arrhenius B , is later discussed,¹² along with an interesting suggestion that values of P differing greatly from unity may be associated with those reactions for which reactants and products have very different "polarities."¹³ Notable exceptions to the principle are cited in the paper, and even more striking ones could be added. For example, the reaction $\text{AsO}_3^{--} + \text{TeO}_4^{--} \rightarrow \text{AsO}_4^{--} + \text{TeO}_3^{--}$, which is polarly symmetrical, has a P value of the order of 10^{-5} instead of approximately unity as required by Soper's rule. We consider, however, that this difficulty has since been removed¹⁴ by making a necessary allowance for the electrostatic contribution to the total free energy change. Although the principle may not yet be regarded as established, there are numerous reactions which conform to it. Quantitative application of the idea of entropy to explain anomalous reaction rates have been made in Soper's most recent work.¹⁵ He considers substance 1 to be converted into substance 2 *via* the formation of a substance x . To each of these is ascribed a thermodynamic probability W_1 , W_2 and W_x . The entropies, S_1 , S_2 and S_x corresponding to the three states are obtained from the general relation $S = R \ln W$ per gram-mole. W_x is clearly less than either W_1 or W_2 . Soper now assumes that the *rate* of conversion of the complex into products is proportional to

$$W_2/W_x = e^{\frac{S_2 - S_x}{R}},$$

and that the rate of reversion of the complex into reactants is similarly proportional to $W_1/W_x = e^{\frac{S_1 - S_x}{R}}$. The relative probability of the reaction going forward from 1 to 2 is accordingly

$$\frac{e^{\frac{S_2 - S_x}{R}}}{e^{\frac{S_2 - S_x}{R}} + e^{\frac{S_1 - S_x}{R}}} = \frac{e^{S_2/R}}{e^{S_2/R} + e^{S_1/R}} \quad (27)$$

giving, for the rate of reaction

$$k_1 = \text{constant} \times e^{\frac{H_1 - H_2}{RT}} \times \frac{e^{S_2/R}}{e^{S_2/R} + e^{S_1/R}} \quad (28)$$

Similar expressions hold for the "break-up factor," and the rate of the reverse reaction; the ratio of the rate constants give an equilibrium constant of correct thermodynamic form. In equation (28), when $S_2 > S_1$, the break-up factor approaches unity; when $S_2 < S_1$, we have

$$k_1 = \text{constant} \times e^{\frac{H_1 - H_2}{RT}} \times e^{-S_1/R} \quad (29)$$

of which the last term may be as small as we please. Omitting the arsenite-tellurate reaction (discussed above) Soper's numerical results, at least as far as bimolecular reactions in solution are concerned, can claim considerable experimental support.

¹² Soper and Williams, *Proc. Roy. Soc., A*, 1933, 140, 59; see also Garner, *Phil. Mag.*, 1925, 49, 463.

¹³ Roberts and Soper, *ibid.*, 1932, 140, 71.

¹⁴ Moelwyn-Hughes, *Proc. Roy. Soc., A*, 1936, 155, 308.

¹⁵ *J.C.S.*, 1935, 1393.

In this connection, the variation with temperature of the Arrhenius energy of activation, E_A , is of some importance. To ascribe numerical values to the entropy of activation from experimental values of $\frac{dE_A}{dT}$ is a somewhat precarious task, because the effect may be due to a number of causes not necessarily related to entropy of activation. An apparent value of $\frac{dE_A}{dT}$ may be due to; (1) The limitations of accuracy in the technique adopted for measuring k , (2) Inaccuracy in the control of temperature, (3) Occurrence of side reactions.

As examples we may quote (1) *The Decomposition of Acetone-dicarboxylic Acid*. Wiig's manometric data (1928) give $E_A = 23,350 \pm 250$ calories. His titration data (1930) give $E_A = 23,200 \pm 500$ calories. These are reasonable limits of accuracy for this technique (Moelwyn-Hughes and Hinshelwood, 1931), hence on the evidence available, $\frac{dE_A}{dT} = 0$ (*Kinetics of Reactions in Solution*, Chapter II., 1933). (2) *The Decomposition of Diacetone-alcohol, Catalysed by Hydroxyl Ion*. At 25° C., Murphy (1931) found $E_A = 17,040$, and at 30° C., $E_A = 18,098$. Hence the apparent value of $\left(\frac{dE_A}{dT}\right)_{27.5^\circ\text{C.}}$ is + 211 calories/degree. La Mer and (Miss) M. L. Miller (1935) find $E_A = 17,250$ at 24.9° C., and $E_A = 17,240$ at 30°, hence $\left(\frac{dE_A}{dT}\right)_{27.5^\circ\text{C.}} = -2$ calories, i.e., virtually zero. (3) The reaction between sodium thiosulphate and sodium bromopropionate. La Mer¹⁶ records a high positive value for $\frac{dE_A}{dT}$. Dawson (1934) and Moelwyn-Hughes (1933) have independently stressed the necessity of allowing for side reactions in this case. Nielsen¹⁷ acting on the suggestion, finds that the correction removes the so-called anomalous salt effect. It is not improbable that the value of $\frac{dE_A}{dT}$ may also be radically altered by introducing the same correction.

These instances have been discussed from a somewhat different angle by La Mer.¹⁸

The least ambiguous case known of a genuine value of $\frac{dE_A}{dT}$ is the inversion of cane sugar.¹⁹

The Frequency of Binary Collisions in Solution.

The subject of chemical kinetics entered an important phase with the appearance of a well-known paper by Eyring and Polanyi in 1931. Within the last year, both authors have independently and almost simultaneously elaborated their theory to cover the case of bimolecular reactions in solutions.²⁰ There is agreement among these authors that the frequency of binary collision in solution is of a higher order of magnitude (being about 100 times greater) than the corresponding frequency for gaseous systems. Since this conclusion differs from an earlier one

¹⁶ *J. Amer. Chem. Soc.*, 1933, 55, 1739.

¹⁷ *Ibid.*, 1935, 58, 206.

¹⁸ *J. Chem. Physics*, 1933, 1, 289.

¹⁹ Moelwyn-Hughes, *Trans. Faraday Soc.*, 1928; *Z. physikal. Chem.*, 1934.

²⁰ Wynne-Jones and Eyring, *J. Chem. Physics*, 1935, 3, 492; M. G. Evans and Polanyi, *Trans. Faraday Soc.*, 1935, 31, 875.

which, though provisional, has been fairly widely accepted, we shall consider the evidence upon which it rests.

According to Wynne-Jones, Eyring, Evans and Polanyi, the velocity constant (k_2) of a bimolecular reaction equals the product of the equilibrium constant (K^*) which governs the formation of the active complex, and a frequency term γ . According to Wynne-Jones and Eyring, $\gamma = kT/h$; according to Evans and Polanyi, $\gamma = \frac{1}{2}v$. In either case, it is supposed not to be markedly influenced by a solvent. Hence, in any system;

$$k_2 = K^* \gamma \quad . \quad . \quad . \quad (30)$$

The equilibrium constant in any dilute system is

$$K^* = \frac{c_{AB}}{c_A \times c_B} \quad . \quad . \quad . \quad (31)$$

Now if Henry's law is obeyed by all three solutes, we have

$$s = c_{\text{solution}}/c_{\text{gas}} \quad . \quad . \quad . \quad (32)$$

where s is the solubility, and

$$K^*_{\text{solution}} = K^*_{\text{gas}} \times \frac{s_{AB}}{s_A \times s_B} \quad . \quad . \quad . \quad (33)$$

which is the familiar equation of van't Hoff.²¹ The similarity with equation (9a) is obvious. Since γ is taken as independent of the medium,

$$k_{2(\text{solution})} = k_{2(\text{gas})} \times \frac{s_{AB}}{s_A \times s_B} \quad . \quad . \quad . \quad (34)$$

Now, it appears that s has the order of magnitude 1/100 for a number of solutes in different solvents.²² If, therefore, the "solubility of the transition state" is assumed to have this value, and if the energy of activation is the same in the two systems, it may be concluded that

$$Z_{(\text{solution})} = Z_{(\text{gas})} \times \text{about } 100 \quad . \quad . \quad . \quad (35)$$

The conclusion is thus based on a number of postulates, including one which invests the reactive complex with a definite solubility. The solubility of a reactive complex, though perhaps conceivable, is not measurable. The conclusion summarised in equation (35) must therefore always rest on purely theoretical foundations.

The earlier observation, to which reference was made above, was based on the experimental comparison of the observed velocities and energies of activation of those bimolecular reactions which have been measured in the gas phase and in solution. Such a comparison suggests that the frequency of binary collisions in the two dilute systems has the same order of magnitude.²³

Choice between the two views will hardly be possible until more extensive applications of both have been tried out. In the meantime, it is a matter of convenience to place side by side the various evidences advanced in their favour.

²¹ Cf. *Kinetics of Reactions in Solution*, p. 131.

²² Cf. M. G. Evans and Polanyi, *Trans. Faraday Soc.*, 1936, **32**, 1333. I have to thank the authors for sending me their MS. before publication.

²³ Cf. *Acta Physicochimica*, U.S.S.R., 1936, **4**, 173.

A Proposed Method of Determining the Entropy of Activation.

Eyring²⁴ deduced the following formula for the velocity coefficient of chemical reactions of any order:—

$$\text{Velocity constant} = \frac{kT}{h} \cdot K^* \quad . \quad . \quad . \quad (36)$$

K^* is a specially defined equilibrium constant, which, for systems undergoing simple motions, can be readily expressed in terms of partition functions. Eyring's general equation, which has proved a stimulus to thought on the subject of reaction kinetics, is particularly attractive in virtue of its generality.²⁵ It may be regarded as a generalisation of Herzfeld's velocity equation (16), in the same sense as Fowler's equilibrium equation²⁶ is a generalisation of Stern's equation (14). On applying equation (36) to the case of bimolecular reactions, Eyring shows (p. 114 of his paper) that the resulting expression reduces to the familiar classical expression, as, of course, it should be if equation (36) is at all general. It is true that the classical result emerges only after certain postulates are made, but these are no more severe than the postulates which underlie the derivation of the general equation (36). Accordingly, Eyring's quantum treatment and the old classical treatment may be regarded as harmonious and complementary.²⁷

The application of Eyring's general theory to the specific problem of bimolecular reactions in solution was undertaken by Wynne-Jones and Eyring,²⁸ who accept the velocity in the gaseous state as a standard. To relate this to the velocity in solution, Henry's law (equation 32) is introduced. This approach is based on reliable experimental foundations, and follows, as we have seen, the scheme proposed by van't Hoff. The complexity of the dissolved state of matter makes it expedient to replace statistical partition functions by thermodynamic variables. The physical picture of the solvent effect is presented in two ways, *vis.* (1) union of solute and solvent molecules to form a larger active complex than is formed in the gas phase, or (2) the motion of the complex or of its constituent parts in a field of force different from that prevailing in the gas phase. "Either treatment simply has the effect of increasing the number of degrees of freedom" (p. 495). Here again, we are on fairly well-beaten tracks. "The rôle of the solvent in chemical kinetics has not yet been definitely correlated with any physical properties, and seems to belong to the category of specific chemical effects, which range from the formation of complexes, on the one hand, to an apparently inert or purely diluent influence on the other. The suggestion can therefore be made that the varying values of F (degrees of freedom) from solvent to solvent may indicate in a quasi-quantitative manner the extent to which the solvent enters into partnership with the reactant for purposes of decomposition."²⁷ A new principle which is employed by Wynne-Jones and Eyring may be enunciated as follows: the reactive complex resembles, or differs from, the products of reaction according as the entropy of activation, ΔS^* (calculated from kinetic data by a method described below) resembles or is different from the entropy of reaction, ΔS (calculated in the usual thermodynamic manner from experimental data on equilibrium constants). Their treatment of bimolecular

²⁴ *J. Chemical Physics*, 1935, 3, 107.

²⁵ *Cf. Annual Reports on the Progress of Chemistry*, p. 94, (1935).

²⁶ *Statistical Mechanics*, p. 106, Cambridge, 1929.

²⁷ Moelwyn-Hughes, *J.C.S.*, 1932, 106.

reactions is based on a quantitative comparison of ΔS^* and ΔS . Their method of calculating the entropy of activation, ΔS^* , is as follows.

Omitting the transmission coefficient, κ , which is throughout the paper taken as unity, the theoretical expression proposed for the bimolecular velocity constant is

$$k_2 = K^* \cdot \frac{kT}{h} \quad (36)$$

$$\text{Substitution of } K^* = e^{-\Delta H^*/RT} \cdot e^{\Delta S^*/R} \quad (37)$$

$$\text{gives } k_2 = \frac{kT}{h} \cdot e^{-\Delta H^*/RT} \cdot e^{\Delta S^*/R} \quad (38)$$

An examination of the figures reproduced under ΔH^* in Table II. (p. 499) makes it clear that ΔH^* is identified with the Arrhenius energy of activation, E_A , hence the theoretical expression for the bimolecular velocity constant is

$$k_2 = \frac{kT}{h} \cdot e^{-E_A/RT} \cdot e^{\Delta S^*/R} \quad (39)$$

The units of entropy, we may infer from Table I. (p. 498), are calories per mole-degree, since Soper's figures, which are there reproduced, are known to be in these units. According to the classical theory, bimolecular reactions with normal velocities have coefficients given by the equation

$$k_2 = \frac{N_0}{1000} (r_1 + r_2)^2 \sqrt{\frac{8\pi kT}{\mu}} \cdot e^{-E_A/RT} \quad (40)$$

The units of k_2 in equation (40) are litres, gram-molecules and seconds. Moreover, for molecules of ordinary masses and radii, the term

$$\frac{N_0}{1000} (r_1 + r_2)^2 \sqrt{\frac{8\pi kT}{\mu}}$$

is known to be about 2×10^{11} litres per gram-molecule-second. We thus have, for bimolecular reactions with normal velocities,

$$k_2 \cong 2 \times 10^{11} \times e^{-E_A/RT} \quad (40a)$$

At ordinary temperatures, kT/h is approximately 6×10^{13} seconds⁻¹, hence the expression of Wynne-Jones and Eyring is

$$k_2 = 6 \times 10^{12} \times e^{\Delta S^*/R} \times e^{-E_A/RT} \quad (39a)$$

Eliminating k_2 and E_A we have $e^{\Delta S^*/R} = Z \cdot \frac{h}{kT} = \frac{2 \times 10^{11}}{6 \times 10^{13}}$ therefore $\Delta S^* = -6.9$. Hence Wynne-Jones and Eyring conclude (p. 499), that "when the reaction rate is just equal to that calculated by Moelwyn-Hughes (*i.e.*, calculated by equation (40)) the entropy of activation is seven units," and that "for a bimolecular reaction at 50-100° C. a kinetic theory collision diameter of 2Å. is equivalent to an entropy of activation of 6.9."

To take a numerical illustration of their theory, we shall apply it to a particular example—the union of triethylamine and ethyl bromide in benzene solution: $(C_2H_5)_3N + CH_3Br \rightarrow (CH_3)_3N \cdot Br$. The experimental results, in litres per gram-molecule-second, may be written in the form:

$$k_2 = 1.47 \times 10^8 \times e^{-11,190/RT}$$

Taking the experimental temperature as 331° Abs., and comparing with

$$k_s = \frac{kT}{h} \times e^{\Delta S^{\circ}/R} \times e^{-11,190/RT}$$

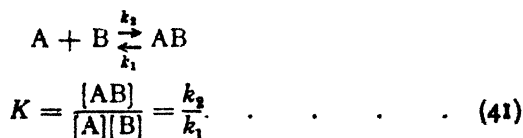
it is found that $\Delta S^{\circ} = -48.8$.

If the theory of Wynne-Jones and Eyring is substantiated, it embodies a new principle, the importance of which has not hitherto been recognised, in that reacting systems differing as widely as the following, *vis.*, $(\text{HI} + \text{HI})$, $(\text{H}_2 + \text{Br})$, (CH_3CHO) and $(\text{NH}_4^+ + \text{CNO}^-)$ have all the same entropy of activation. The validity of the theory has, however, been challenged²⁸ and further defended.²⁹ The criticism draws attention to the dimensions and units of k_s in equation (39). The reply deals with the subtraction of certain constants which is necessary when ΔS and ΔS° are compared, but to which no reference can be found in the original work. A recalculation of the published figures shows, however, that the constant in each case is zero. While this difference of opinion continues, the matter must be considered *sub judice*.

The Influence of Pressure on the Kinetics of Reactions in Solution.

Fawcett, Gibson, Perrin and Williams³⁰ have recently studied the influence of high pressure on the velocity of numerous reactions in solution, which had previously been examined under ordinary conditions. Our experimental knowledge has thereby widened considerably from the somewhat narrow limits which formed the basis of our previous discussion of this subject.³¹

The general outline of the theory of the pressure effect has been given by van't Hoff,³² whose treatment we shall here reproduce, using the newer notation of Lewis and Randall. Consider the equilibrium



We employ the two thermodynamic relations

$$\Delta F = -RT \ln K \quad . \quad . \quad . \quad (42)$$

$$\text{and} \quad \Delta F = \Delta E + P\Delta V - T\Delta S \quad . \quad . \quad . \quad (43)$$

$$\text{which give us} \quad \left(\frac{d \ln K}{dP} \right)_T = - \frac{\Delta V}{RT} \quad . \quad . \quad . \quad (44)$$

van't Hoff points out that this equation is in satisfactory agreement with results on the pressure-coefficient of the electromotive force of a reversible cell. Qualitatively, the principle may be stated as follows:

²⁸ Moelwyn-Hughes, *J. Chemical Physics*, 1936.

²⁹ Wynne-Jones and Eyring, *ibid.*, 1936.

³⁰ Fawcett and Gibson, *J.C.S.*, 1934, 386; Gibson, Fawcett and Perrin *Proc. Roy. Soc., A*, 1935, 180, 223; Williams, Perrin and Gibson, *ibid.*, 1936, 184, 684.

³¹ *Kinetics of Reactions in Solution*, p. 256, 1933.

³² *Vorlesungen über theoretische und physikalische Chemie*, 1, 236, Braunschweig, 1901.

a reaction which is associated by a decrease in volume (*i.e.*, ΔV is negative) is favoured by an increase in pressure, and *vice versa*. So far, we are on purely thermodynamic grounds, limited by the provision that ΔV does not depend on the pressure. We may go one stage further in the general argument. By definition

$$\Delta V = V_2 - V_1 \quad . \quad . \quad . \quad . \quad (45)$$

where V_1 is the volume of the initial system, and V_2 that of the final system. This equation may also be written as

$$\Delta V = (V_2 - V^*) - (V_1 - V^*) \quad . \quad . \quad . \quad . \quad (46)$$

in which V^* is an arbitrary volume. Combining with equations (41) and (44), we have

$$\left(\frac{d \ln k_2}{dP}\right)_T - \left(\frac{d \ln k_1}{dP}\right)_T = -\frac{(V^* - V_1)}{RT} + \frac{(V^* - V_2)}{RT} \quad . \quad (47)$$

The resolution of this equation into two separate ones, purporting to hold independently for the direct and reverse reactions, is again an assumption, which may or may not be vindicated by its consequences. The splitting up of equation (47) is equivalent to giving V^* an unique, as distinct from an arbitrary, value. Making the assumption, we obtain

$$\frac{d \ln k_2}{dP} = -\frac{(V^* - V_1)}{RT} \quad . \quad . \quad . \quad . \quad (48)$$

and

$$\frac{d \ln k_1}{dP} = -\frac{(V^* - V_2)}{RT} \quad . \quad . \quad . \quad . \quad (49)$$

These relations imply that the velocity k_2 of chemical reaction increases on raising the pressure, provided the volume, V^* , of the active molecules (in the Arrhenius sense) is less than the volume, V_1 , of the reactants. van't Hoff concluded that the data available to him were insufficient to test these equations.

Williams, Perrin and Gibson³⁰ find equation (49) to be obeyed in the case of the reaction between acetic anhydride and ethyl alcohol in toluene solution at 40° C., up to pressure exceeding 8000 kilograms per sq. cm. The agreement in the second example given by them (reaction between pyridine and ethyl iodide in acetone solution) is approximate only.

Just as the temperature coefficient of any velocity constant is best reflected by the (Arrhenius) energy of activation, E_A , the pressure coefficient is most conveniently shown by the volume change attending the conversion from normal to active molecules. In Table I. we give

TABLE I.

Reaction.	Solvent.	$(V^* - V_1)$ c.c. Per Gram-mol.
Hydrolysis of methyl acetate, catalysed by N. HCl	Water . .	— 9.0
Hydrolysis of sucrose, catalysed by N. HCl . .	Water . .	+ 2.7
Reaction between acetic anhydride and ethyl alcohol	Ethyl alcohol	— 16.5
" " "	Toluene . .	— 12.5
" " "	Hexane . .	— 4.16

the values for the volume increase ($V^* - V_1$) calculated for certain reactions by means of equation (49). The velocity constant and pressure data for the first two reactions are cited by van't Hoff;³² the corresponding figures for the remaining reactions are those recently determined by Fawcett, Gibson, Perrin and Williams.

It is now a matter of interest to study these figures in the light of the molecular statistics of the various reactions. Which of them we regard as fast or slow, depends, of course, on the collision frequency which we consider appropriate. If we accept the conclusions of Evans and Polanyi,³³ the hydrolysis of sucrose may be regarded as having a normal rate, the others exhibiting varying degrees of slowness. If we accept the gas kinetic value, or, at least, a figure of that order of magnitude, the hydrolysis of sucrose must be regarded as rapid,³³ the hydrolysis of methyl acetate as slow,³⁴ and the reaction between acetic anhydride and ethyl alcohol also as slow.³⁵ Gibson, Fawcett and Perrin³⁰ noted that the velocity of the slow reactions which they studied (adopting the gas-kinetic collision frequency as a standard) was increased by raising the pressure, and that a reaction with normal velocity (judged on the same basis) was much less influenced. We cannot reproduce ($V^* - V_1$) for that reaction, because equation (49) is not obeyed. In view of these findings, particular interest attaches to the positive value of ($V^* - V_1$) obtained from Röntgen's data for the velocity of the inversion reaction (Table I.). If we adhere to the same definition of normal velocity, we see that the only negative pressure coefficient hitherto recorded for a bimolecular reaction in solution refers to a reaction which is very fast.

A comparison of calculated rates with the experimental values found for the unimolecular decomposition of phenylbenzylmethylallylammonium bromide in chloroform solution showed the reaction to belong to the "fast" group.³⁶ Williams, Perrin and Gibson³⁰ find the coefficient dk_1/dP to be negative.

As far as the accurate, though not very extensive, evidence admits of a conclusion, it is that the van't Hoff relation (49) represents with fair accuracy the majority of the results. Moreover, bimolecular reactions which belong to the slow class have a positive coefficient dk/dP ; bimolecular and unimolecular reactions belonging to the fast class have a negative coefficient dk/dP . The two reactions belonging to the normal class which have been examined are these between ethyl iodide and sodium ethoxide, and between sodium chloracetate and sodium hydroxide. Upon these, the effect of pressure, though not zero, is very slight, e.g., a pressure of 3000 kilograms/sq. cm. roughly doubles the rate. In both cases, it must not be overlooked that some of the reacting ions are in equilibrium with the solvent, giving, for example, undissociated molecules of chloracetic acid and of sodium ethoxide. Since these are themselves capable of reacting, it is possible that the slight influence of pressure on the reacting system affects first the equilibrium constant, and alters the observed velocity indirectly.

Special mention must be made of the value ($V^* - V_1$) = + 2.7 c.c. found from Röntgen's data on the inversion of cane sugar. In the first

³² Moelwyn-Hughes, *Trans. Faraday Soc.*, 1929, 25, 81.

³³ Christiansen, *Z. physikal. Chem.*, 1924; 113, 35; Moelwyn-Hughes, *Phil. Mag.*, 1932, 14, 112.

³⁴ Moelwyn-Hughes and Hinshelwood, *J.C.S.*, 1932, 230; Moelwyn-Hughes and Rolfe, *ibid.*, p. 241.

³⁵ von Halban, *Ber.*, 1908, 41, 2417; Moelwyn-Hughes, *J.C.S.*, 1932, 95.

place, we note that, according to van't Hoff's theory, the volume, V^* , of the reactive complex must be greater than the combined volumes, V_1 , of the hydrated sucrose molecule and the hydrated hydrogen ion. Structural organic chemistry has shown⁸⁷ that the reaction entails the opening of a furanose ring, and the subsequent closing of the chain-like structure into a pyranose ring. This conclusion is consistent with our deduction, and suggests that not only the reactive complex but the final products also may have a larger volume than the initial reactants. In the second place, we estimate the total dilatometric change in volume $\Delta V = (V_2 - V_1)$ accompanying the inversion of one gram-molecule of sucrose in a 20 per cent. solution at 15° C. to be + 1.9 c.c. (Data of Fresenius in Landolt-Börnstein's Tables.) By equation (46), we have $(V^* - V_2) = + 0.8$ c.c. If equation (49) holds, the rate of the catalytic synthesis of sucrose must also be influenced by hydrostatic pressure—a circumstance which may partly account for the inadequacy of the ordinary methods of organic chemistry to accomplish this synthesis.

A Reformulation of the Methods of Introducing Thermodynamic Variables into Expressions for Reaction Velocity Constants.

As a starting-point we have to select the most plausible assumption from the large number that have been made. We shall assume, with most investigators, that the velocity of reaction is proportional to the number of molecules or of complexes for which the (Helmholtz) free energy, F , has reached a certain critical value. Hence, by analogy with equation (42),

$$k = \text{constant} \times e^{-\Delta F^*/RT} \quad (50)$$

Introducing equation (43), we obtain the relation

$$k = \text{constant} \times e^{-\Delta F^*/RT} \cdot e^{-P\Delta V^*/RT} \cdot e^{\Delta S^*/R} \quad (51)$$

where Δ denotes the difference between the property for the passive and active molecules. Applying this relation to the case of bimolecular reactions, we shall accept the view advanced by Rodebush that the undetermined constant of equation (51), multiplied by a term $e^{\Delta S_1^*/R}$, represents the thermodynamic equivalent of the collision frequency. We then have

$$k_2 = Z_2 e^{-\Delta F^*/RT} \cdot e^{-P\Delta V^*/RT} \cdot e^{\Delta S_1^*/R} \quad (52)$$

ΔS_1^* is the remaining fraction of the entropy change. This step differs fundamentally from that taken by Wynne-Jones and Eyring. Our knowledge of the increase, ΔE^* , in internal energy associated with the change from ordinary to activated molecules, is derived, as Arrhenius showed, from the temperature variation of k_2 . Similarly, our knowledge of the increase, ΔV^* , in volume associated with the same change, is derived, as van't Hoff showed, from the pressure variation of k_2 . By elimination, it should be possible to learn something of the product $Z_2 e^{\Delta S_1^*/R}$, and by induction, to ascribe a value, if not a meaning, to the "entropy of activation," ΔS_2^* . Equation (52) gives directly van't Hoff's equation for the influence of pressure on the reaction velocity (equations 48 and 49); when ΔV^* is zero, we have an equation of the form proposed by Soper (equation 28), and elaborated by La Mer. Equation (52) differs from that of Wynne-Jones and Eyring in that they use the

⁸⁷ Haworth, *Constitution of the Sugars*, 1929; Armstrong and Armstrong, *The Glycosides*, 1935.

frequency kT/h instead of the collision frequency Z_2 ; in other words, their evaluation of what we have termed ($\text{constant} \times e^{\Delta S_1^*}$) differs from that of Rodebush, and from that given in Eyring's general theory.

Let us now consider a case of symmetrical equilibrium,³⁸ such as exists between α -glucose and β -glucose in water. The heat effect is too small to be detected by ordinary calorimetric methods; the equilibrium constant, K , is unaffected by temperature and, to the best of our knowledge, the volume change is zero, i.e., $\Delta V = V_\beta - V_\alpha = 0$. Accordingly, pressure should have no effect on equilibria of this kind. Experiments have not yet, however, been directed to test this conclusion of van't Hoff's³⁹ "*Bei Reaktionen ohne Volumenänderung fiel also diese Faktor [$P\Delta V$] weg und so wäre auch hier die gegenseitige Verwandelung von optischen Isomeren z.B. der theoretisch einfache Fall*" (p. 237).³² At atmospheric pressure, the significance of the kinetics of these simple reactions has not been overlooked. They all have velocities equal to those given by the expression

$$k_2 = Z_2 \cdot e^{-E_A/RT} \quad (53)$$

in which E_A is the Arrhenius energy of activation and Z_2 is the gas-kinetic collision frequency.⁴⁰ From equation (52), it follows that ΔS_2^* for these reactions is zero. According, however, to the theory of Wynne-Jones and Eyring, "where the reaction rate is just equal to that calculated by Moelwyn-Hughes (i.e., by equation (53)) the entropy of activation is seven units" (i.e., seven calories per gram-molecule per degree). As mentioned above, we have no information about the volume change ΔV^* in these cases. Should experimental work on the pressure effect confirm van't Hoff's view, we may conclude from equations (52) and (53) that $\Delta E^* = E_A$, i.e., the Arrhenius energy of activation for these reactions gives a direct measure of the increase in internal energy associated with the conversion from normal to active states. An assumption of this nature has, of course, underlain all attempts at determining the absolute rate of reactions in solution. In questioning the validity of the Arrhenius assumption, La Mer has omitted all reference to isomeric reactions.

Let us finally re-examine the pressure effect in the light of equation (52). Comparing it with the semi-empirical relation

$$k_2 = p \cdot Z_2 \cdot e^{-E_A/RT} \quad (54)$$

we obtain the relation

$$E_A = \Delta E^* + P\Delta V^* \left\{ 1 - T \left(\frac{d \ln \Delta V^*}{dT} \right)_P - T \left(\frac{d \ln P}{dT} \right)_P \right\} \quad (55)$$

³⁸ *Kinetics of Reaction in Solution*, Chapter V.

³⁹ Dr. Gibson explained to me some years ago the nature of the technical difficulties which it has not yet been possible to overcome.

⁴⁰ "Mutarotation of Glucose in Water," Moelwyn-Hughes, *Phil. Mag.*, 1932, 14, 112; "Mutarotation of Beryllium Benzoylcamphor in Carbon Tetrachloride Solution," Lowry and Traill, *Proc. Roy. Soc., A*, 1931, 132, 398; Traill, *Phil. Mag.*, 1932, 14, 225; "Beckmann transformation of Benzophenoneoxime Picryl Ether," A. W. Chapman, *J.C.S.*, 1934, 1550; *ibid.*, 1935, 1223; "Mutarotation of Glucose in Heavy Water," Moelwyn-Hughes, Bach and Bonhöffer, *Z. physikal. Chem.*, A, 1934, 469, 113; Moelwyn-Hughes, *ibid.*, B, 1934, 26, 272.

⁴¹ Hildebrand, *Solubility*, 1924, p. 102 1st Ed.

$T\left(\frac{dP}{dT}\right)_P$ may be identified with the internal pressure,⁴¹ hence

$$E_A = \Delta E^* + P\Delta V^* \left\{ 1 - T \left(\frac{d \ln \Delta V^*}{dT} \right)_P \right\} - \pi \Delta V^* \quad (56)$$

The internal pressure for pure acetone is about 5.8×10^9 dynes/cm.², and for ethyl alcohol about 13×10^9 . A hydrostatic pressure of 3000 kilograms per sq. cm. is 2.94×10^9 , so that under high pressure conditions π and P are commensurate. Whether the Arrhenius energy of activation, E_A , increases or decreases as the pressure is raised depends on the sign of the volume increase, ΔV^* , and on the sign of the term inside the bracket. Unfortunately, $\left(\frac{dV^*}{dT}\right)_P$ is not known, but the variation with temperature (without the restriction of constant pressure)

TABLE II.

Temperature (°C.).	ΔV^* (c.c.).	$\left\{ 1 - T \frac{d \ln (\Delta V^*)}{dT} \right\}$.
Reaction between Pyridine and Ethyl Iodide in Acetone		
30	- 16.52	+ 2.90
40	- 17.57	+ 2.79
50	- 18.59	+ 2.72
60	- 19.59	
Reaction between Acetic Anhydride and Ethyl Alcohol in Ethyl Alcohol		
20	- 16.83	- 0.66
30	- 15.92	

of van't Hoff's ΔV^* may be found from experimental data. They are shown in Table II. It is of interest to observe that for these two reactions the term within the brackets has opposite signs; so also has the experimental coefficient dE_A/dP . The corresponding expression for p (equation 54) can be readily obtained.⁴² An attempt to determine either ΔE^* or P numerically requires a knowledge of quantities which are not yet available, as, for example, the value of $\left(\frac{dP}{dT}\right)_P$ for the reacting

system (as distinct from the solvent), and the functional relationship of π to P .

The logical introduction of thermodynamic expressions into the study of reactions kinetics can thus yield information concerning properties of active molecules, other than the energies and volumes, with which Arrhenius and van't Hoff were primarily concerned.

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⁴² See Moelwyn-Hughes, *Proc. Roy. Soc., A*, 1936, **155**, 308.

FORMATION OF DEHYDRATION NUCLEI ON CRYSTALS OF CHROME ALUM.

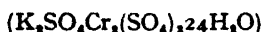
BY J. A. COOPER AND W. E. GARNER.

Received 12th October, 1936.

Nuclei formed on the surfaces of isotropic material are usually circular in shape, growth in this case being uniform in all directions along the surface. Where, however, there are marked divergences between the rates of growth for different directions in the crystal, the nuclei may possess a complex outline, as was found for $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, where they are star-shaped on the surface of the (110) plane,¹ and ² for $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, where they are elongated discs. The conditions under which nuclei form and grow in size have already been investigated ^{1, 2} in some detail for crystals of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, and in these cases it has been shown that there is an induction period before the nuclei become visible, and this has been ascribed to an abnormally slow rate of growth of the nuclei when very small. It is possible that induction periods in solid reaction occur only when the nuclei possess a complex irregular shape, and not at all when the nuclei are spherical. This might be the case if the strains set up by uneven growth of the nuclei were responsible for the acceleration of the rate of nuclear growth. It was therefore important to carry out an investigation on some hydrate where the rates of growth in all directions were the same, and crystals of chrome alum have been chosen for this purpose.

Experimental.

A saturated solution of Kahlbaum's " Puriss " Chrom Alum



was made in distilled water, and this was allowed to crystallise in an air thermostat under such conditions that the solutions were protected from dust. The surfaces of the crystals were very delicate, and it was found to be impossible to employ the method of drying adopted previously with copper sulphate for they become scratched under this treatment. Also, the method of draining used by Garner and Southon was found to be ineffective in this case. The method finally adopted was to remove the crystals from solution and place them for a very short time in distilled water (about 1 second) and then place one face of the crystal on soft filter paper. This ensured that drying occurred without scratching. So prepared, the crystals could be stored in a desiccator over powdered chrome alum for several weeks without decomposition occurring.

The vessel used for the study of nuclei formation was the same as that used previously. The crystals were exposed to a high vacuum, which is attained within a few seconds of applying the pump, and the nuclei formed are observed either visually or photographs are taken of them at suitable intervals of time. In most cases 15 to 20 photographs were taken during the course of a single experiment. Usually about 50 nuclei were formed within the field of vision of the cathetometer.

¹ Bright and Garner, *J.C.S.*, 1934, 1872.

² Garner and Southon, *J.C.S.*, 1935, 1705.]

Experimental Results.

The nuclei are circular in shape, as would be expected for a cubical crystal (Fig. 1), but since the rate of growth into the interior is not so rapid as along the surface, due to retardation of the escape of water through the varying thicknesses of the dehydrated product, the nuclei actually consist of flattened half spheres. At an early stage in the growth of a nucleus, a cavity forms in its centre, and this is well shown in Fig. 1. The nuclei possess a diffuse and somewhat irregular edge, indicating that the area of the interface between the hydrate and its product is quite large. There are differences between the rates of growth in different directions along the surface, but these are, however, small and of the order of 2-4 per cent. The lack of uniformity in the growth suggests that there are discontinuities within the crystal lattice.

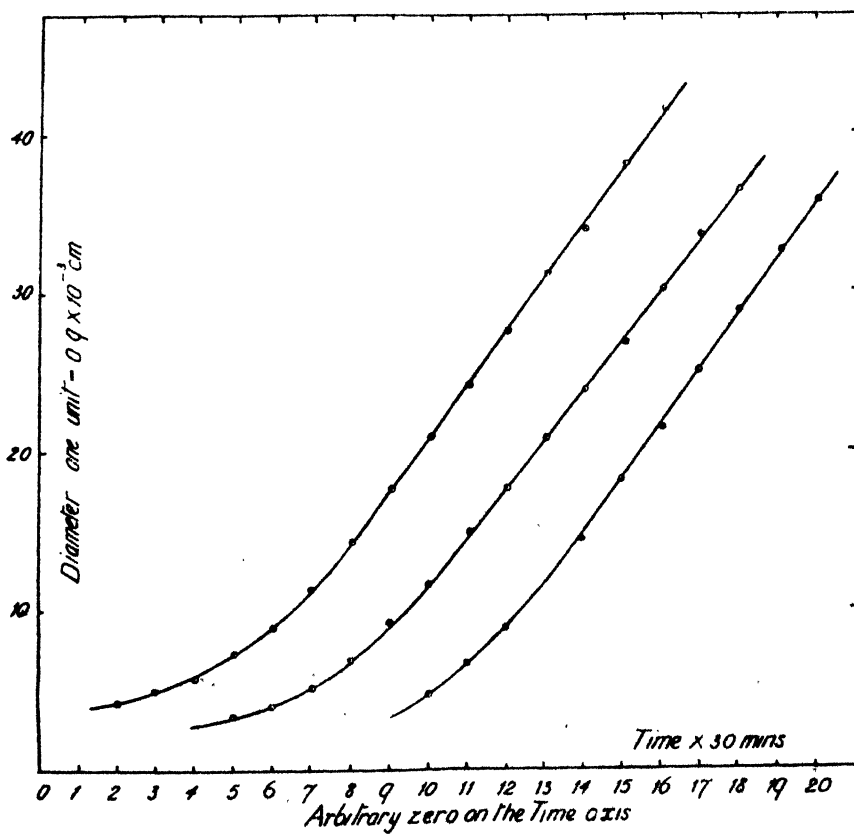
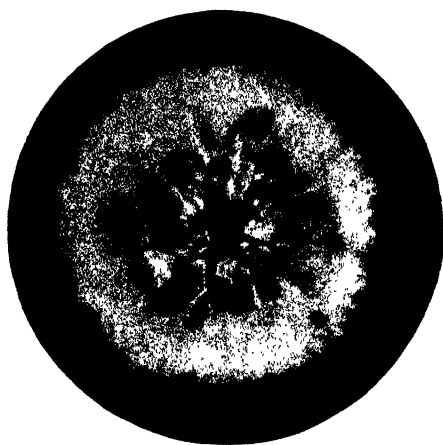


FIG. 2.

Rates of Growth of Nuclei.

Measurements of the rates of growth made visually indicated that the nuclei grow abnormally slowly when small, and do not increase in size at a linear rate until they are above 10^{-3} cm. in diameter. It was therefore decided to carry out measurements by the photographic method in order to measure accurately the changes in the rates of growth of the nuclei. About twenty exposures are taken of a dehydrating crystal at suitable intervals of time, and for each crystal, ten nuclei are chosen, and the diameters of these measured on each exposure. For each nucleus a plot



0.4 mm. diameter.



Magnification 3.

FIG. 1.

[To face page 1740.]

is made of the size against time and in order to obtain greater accuracy, the plots for the ten nuclei are combined in a composite curve. The origin of the nuclei on the time axis varies from case to case, and in order to obtain the composite graph it is assumed that the nuclei always require the same time to reach a particular size. The assumption appears to be justified both by the photographic and visual observations. Three composite curves are shown in Fig. 2, and it will be seen that the rate of growth is exponential at first, becoming linear above 10^{-3} cm.

Rate of Nucleus Formation.—A number of measurements have been made at 14° C. of the increase in number of the nuclei with time. After an induction period of about 30 minutes, the increase in number was practically linear (Fig. 3 A), as was found previously for $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. The behaviour is, however, in sharp contrast with that of nuclei on

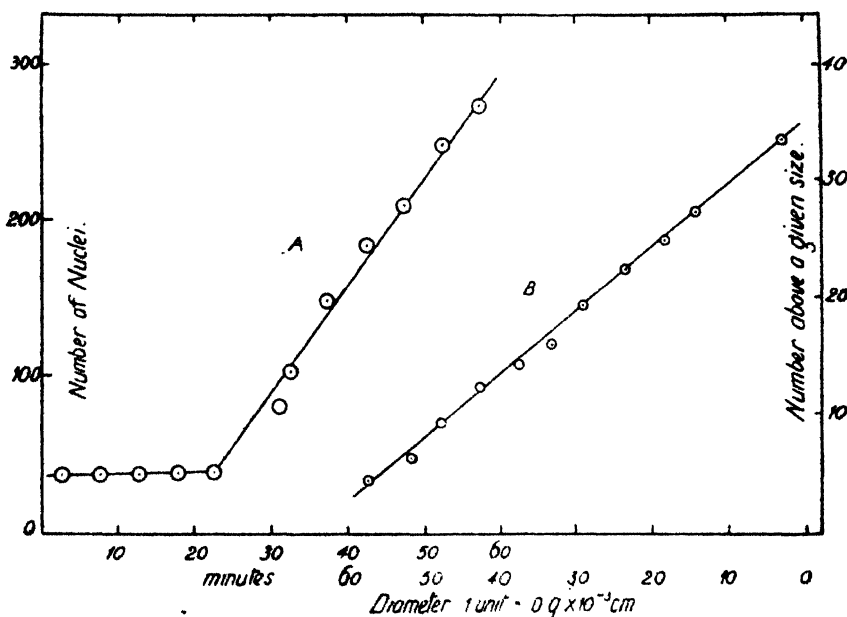


FIG. 3.

where the number increases as the square of the time. The induction periods were not, however, very reproducible, so that no attempt was made to measure temperature coefficients.

It has been shown that the nuclei grow at a linear rate when above 10^{-3} cm. in diameter, so that the size of any nucleus is a linear function of the time which has elapsed since it started to grow at a linear rate. Therefore, if the diameters of all of the nuclei be measured at any fixed time, as can be done from the photographs of the dehydrating crystal, and the number above a given size be plotted against size, a graph should be obtained of the same form as that obtained when plotting number against time. This is done in Fig. 3 B, and a linear relationship is seen to be obtained for the nuclei above 10^{-3} cm. in size. This confirms the conclusion that the number of nuclei increases linearly with the time.

Discussion.

The slow rate of growth of small nuclei as shown in Fig. 2 is of considerable importance for the interpretation of the nature of induction

periods in solid reactions, and it is therefore worth while considering the theoretical significance of these slow rates of growth.

A possible explanation of the phenomenon is that it is due to a negative tension set up in the interface by the tendency to contraction of the product. If this tension is constant, the problem may be treated thermodynamically, as was done by Kelvin to account for the change in vapour pressure with variation in the radii of small drops. For small drops, $RT \log_e p/p_0 = 2MS/r\rho$, where p is the vapour pressure of a drop of radius r , p_0 the ordinary vapour pressure, and M the molecular weight of the vapour, S the surface tension, and ρ the density of the liquid. In the case of a nucleus on the surface of a crystalline hydrate,

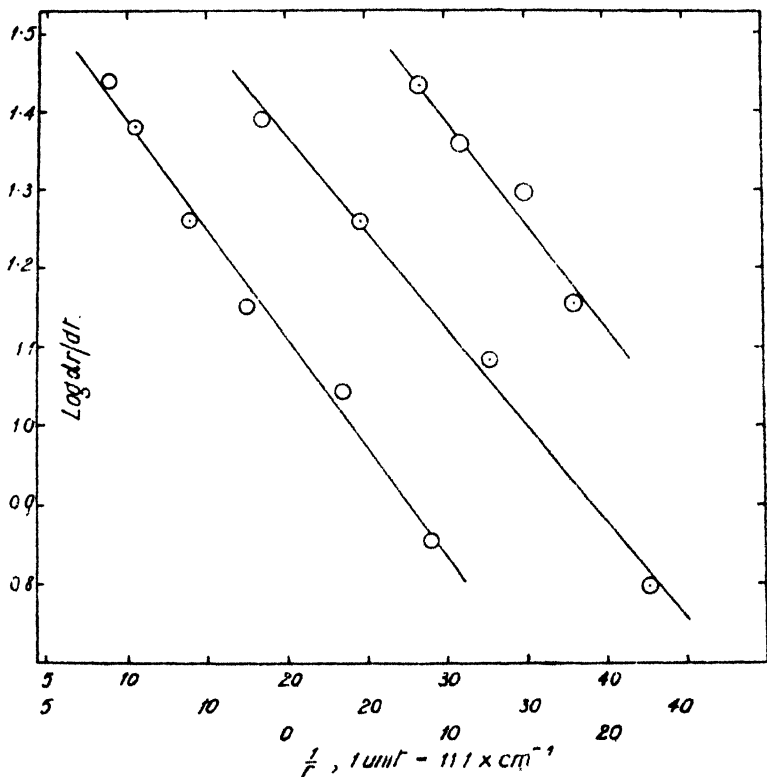


FIG. 4.

p is the dissociation pressure of water vapour at the interface for a nucleus of radius r , p_0 the ordinary dissociation pressure for a plane surface and S the tension in the interface, and since M , S , T , ρ and p_0 are constants,

$$RT \log p = K_1/r + K_2,$$

which gives the variation of the dissociation pressure with curvature.

Now the rate of growth of the nuclei in hard vacuum is proportional to the rate of evaporation of water molecules from the interface, and since the latter is proportional to the dissociation pressure it follows that

$$RT \log dr/dt = K_1/r + K_2'$$

and the graph of $\log_{10} dr/dt$ against $1/r$ should give a straight line. Such plots are given in Fig. 4 for the nuclei observed on three films and

within the experimental error it will be seen that there is agreement with the thermodynamic argument. Three values of the slope k are obtained, -2.83 , -2.37 , -2.83×10^{-8} , which give a mean value of

$$-2.68 \times 10^{-8} \text{ cms.}$$

Since $k = \frac{2mS}{2.303 RT \rho}$, it is seen that $S = 7.49 \times 10^6$ dynes/cm., which compared with the surface tension of water (75 dynes/cm.), is a very large tension. It would give rise to pressure differences in the case of the nuclei of the diameters on which the measurements were made of many tons per sq. in.

The thermodynamic relationship holds only over the curved portion of Fig. 2, and breaks down before the rate of growth becomes constant. It is, therefore, necessary to make the additional postulate that the tension ceases to be constant when the particles reach a certain size, and this may well be the case for the contraction of the material of the nuclei giving rise to the cavities and cracks visible in the photographs would cause a diminution of the tension. It is also necessary to assume that the nuclei originate at centres of disturbance which are much larger than molecular dimensions, otherwise it would be impossible to account for the observed lengths of the induction periods. All that can be said at the moment is that this thermodynamical argument is not incompatible with the results observed.

It can be tested further, for one requirement of the theory is that the dissociation pressure of a small nucleus should be less than that of a large nucleus. In which case, it should be possible to check the growth of small nuclei at lower vapour pressures than for large nuclei. Measurements are now being made to investigate this matter.

Tests have been made of the applicability of other equations, *viz.*,

- (1) $dr/dt = k_1 - k_2 r$, (2) $dr/dt = k_1 - k_2/r^2$,
 (3) $dr/dt = kr^2/(r^2 + k)$, (4) $dr/dt = kr/(r + k)$,
 (5) $dr/dt = k_1 + k_2 r$ and (6) $\log r = kt + \text{const.}$,

and except for (3) which gives a very good fit over the whole curve and (6), which gives a fit over the curved portion of Fig. 2 only, the equations are not in agreement with the experimental results. The agreement with equation (3) is, however, very good. It can be tested by means of the integrated form of this equation (3) giving the variation in r with time,

$$t = \frac{r^2 + Ar - B}{Cr}$$

and the values of t calculated in this way are compared with the experimental values in Table I.

This is the only equation we have found which is in agreement with the complete experimental curves.

It is, however, an empirical equation, and up to the present it has not been linked up with a physical explanation.

The rate of decomposition of certain solids which decompose with evolution of heat, *viz.*, mercury fulminate, barium azide, and potassium azide, changes very rapidly with the time. Thus for mercury ful-

TABLE I.

t (exp.).	t (calc.).
19	18.9
18	18.0
17	17.0
16	16.0
15	15.0
14	14.0
13	12.9
12	11.9
11	10.9
10	9.94
9	8.9
8	8.0
7	6.9
6	5.96
5	4.99
4	3.9
3	3.0
2	2.2
1	0.97

minate the rate varies as the twentieth power of the time. It is not possible to account for these facts in terms of solid nuclei growing at a linear rate from the moment of origin, and it has been suggested previously either that the reactions are chain reactions, or that the nuclei when very small grow at an accelerating rate. It has not been found possible to decide between these two theories in the case of exothermic changes for no nuclei have been found in such cases which are susceptible of accurate measurement of their rates of growth. The above experiments with chrome alum do, however, show that the cause of the marked induction periods in these exothermic decompositions may lie in the lack of linearity in the rate of growth of small nuclei.

Summary.

Measurements have been made of the rates of growth of the spherical nuclei formed on dehydration of crystals of chrome alum. The nuclei have been shown to grow at an accelerating rate up to 10^{-3} cm., and then to increase in size at a linear rate. The causes underlying the accelerating rate of growth are, however, obscure. The presence of a tension in the interface depressing the dissociation pressure would, however, account for the results obtained, and on applying the Kelvin equation a value of 7.49×10^6 dynes/cm. is obtained for the tension. The bearing of the results on the induction periods in solid reactions is discussed.

Our thanks are due to Imperial Chemical Industries Ltd. for a grant.

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ADSORPTION OF CARBON MONOXIDE ON ZINC OXIDE.

BY W. E. GARNER AND J. MAGGS.

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The adsorption processes occurring on porous bodies often require lengthy periods for the establishment of equilibrium. In the case of some metals and simple crystalline salts, the adsorption is separable into two processes, (1) an initial rapid process believed to occur on the readily accessible areas of the adsorbent, and (2) a slow process due to diffusion of the gas down capillaries of molecular size, the rate of which obeys the diffusion equations and is also proportional to the degree of saturation of the gas on the readily accessible areas.¹ The sharp separation into two processes is possible only for certain types of porous body. For precipitated oxides, for example, there is a tendency for the two processes to be merged into one, probably due to a continuous gradation in the size of the pores. In such cases, it is generally found that the diffusion equations do not hold exactly and that the deviations which occur from these equations are affected by conditions which modify the pore diameters, such as sintering, etc.

¹ Ward, *Proc. Roy. Soc., A*, 1931, 133, 522; Bradley, *Trans. Faraday Soc.*, 1934, 30, 587.

The occurrence of capillary flow makes the investigation of adsorption on porous bodies very difficult, especially when information is sought regarding the activation energy of such processes. Activation energies derived from rates of adsorption are always of doubtful value if capillary flow is present, for it is uncertain to what extent the activation energy is that of the adsorption process itself or that of surface flow.² It is therefore of interest to study the adsorption of gases under such conditions that complications due to capillary flow are at a minimum. Such conditions were observed during the adsorption of carbon monoxide and dioxide on a specimen of zinc oxide. It was found that the adsorption was practically instantaneous at room temperature and that the secondary slow adsorption was practically absent.³ Experiments have been made with this oxide to determine if the adsorption processes, which give heats of adsorption 12-18 K. cal./mol., possess activation energies. With this purpose in view, the adsorption isobar was studied to find out whether or not a minimum was present.⁴ In addition, it was sought to check the values for the heats of adsorption as determined in the thermocouple calorimeter.

Experimental.

Carbon monoxide was prepared from formic acid and sulphuric acid and the zinc oxide used was that employed previously.³ The oxide, which was in granular form, was contained in a platinum gauze cylinder suspended in the centre of the adsorption vessel by means of fine tungsten wire hooks sealed into glass. The weight of oxide was 2.21 gm. The adsorption vessel was connected through a liquid air trap to gas burettes, McLeod and Pirani gauges and high vacuum pumps. The volumes of various parts of the apparatus were determined with helium gas.

The oxide was baked out in a high vacuum at 460° C. for two hours before each experiment and after cooling to room temperature was placed in a bath kept at constant temperature. The temperatures ranged from that of liquid oxygen up to 40° C. When the adsorbent had attained a constant temperature, a known volume of carbon monoxide was admitted from the gas burettes, and readings taken of the pressure after five and twenty minutes respectively. Equilibrium was always attained within five minutes except for the lowest temperatures, provided that the oxide was in thermal equilibrium with the surroundings.

Adsorption Isotherms.

The adsorption isotherms were determined by the admission of successive quantities of carbon monoxide. It was not found possible to control the baking out so as to ensure that the surface of the oxide was in exactly the same state for each experiment so that it was advantageous after each baking-out to make adsorption measurements at two temperatures. This was done in the determinations of the heats of adsorption between 0° and 20° C. Except at very low pressures and low temperatures, the plot of $\log p$ against \log amount adsorbed gave a good straight line, so that the experimental results were in good agreement with Freundlich's equation. The results of two typical experiments are given in Fig. 1 for the oxidised and reduced zinc oxide respectively. The first two measurements in each experiment were made at 20° C., the next two at 0° C., the next at 20° C., and so on. The reduction of the oxide with

² Cf. Lennard-Jones, *Trans. Faraday Soc.*, 1932, **28**, 433.

³ Cf. Garner and Veal, *J. Chem. Soc.*, 1935, 1436, 1487.

⁴ Cf. H. S. Taylor, *J.A.C.S.*, 1931, **53**, 578.

hydrogen or its oxidation with oxygen had but a slight effect on the

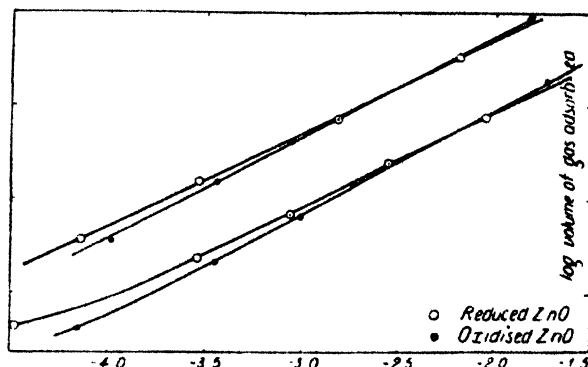


FIG. 1.

amounts of gas adsorbed or on the heat of adsorption. Also, the presence or absence of mercury vapour was found to have but a slight effect on the nature of the results; the amount of gas adsorbed was greater in the absence of mercury vapour but the heats of

adsorption were unaffected.

Heats of Adsorption.

The heats of adsorption were calculated from the adsorption isotherms with the aid of the Clausius-Clapeyron equation. Typical results for the untreated zinc oxide, reduced and oxidized zinc oxide are given in Table I. for the temperature interval 0-20° C. Mercury vapour was present in these cases in order that the results should be strictly comparable with those determined in the thermocouple calorimeter, where mercury vapour was also present.

It will be noted that the heats do not change appreciably with the amount of gas adsorbed.

The surface of the catalyst was as nearly as possible in the same state as that employed in measurements of the heats of adsorption in the thermocouple calorimeter and hence the above results should be directly comparable with those of Garner and Veal. The experimental heats varied with the amount of gas adsorbed, that is, with the gas pressure above the oxide. Between 0 and 2×10^{-3} cm. pressure, $Q = 18.2$ and between 2 and 8×10^{-3} cm. $Q = 12.5$ K. cal./mol. The heat of adsorption calculated by the thermodynamic method does not include that of the first small quantities adsorbed and these heats will therefore not be comparable with the first of the above values. The second, however, was determined within the same range of equilibrium pressures as the thermodynamic heats and the agreement is within the experimental error of the direct method.

TABLE I.

Log Amount Adsorbed (c.c.).	Q Untreated.	(K. Cal./Mol.).	
		Oxidized.	Reduced.
-1.8	—	13.28	14.08
-1.6	14.20	13.74	14.72
-1.4	13.56	13.95	14.26
-1.2	13.54	13.50	14.26

Heats of Adsorption at Lower Temperatures.

Two or three readings were made of the adsorption at 0° C. and these were followed by measurements to obtain the adsorption isotherm at some other fixed temperature. The conditions of baking out were kept as constant as possible but it was found necessary to make corrections to bring the curves to the same condition of the surface. The results obtained are given in Table II.

TABLE II.

Temp. ° K.	Log. Amount Adsorbed when log Pressure is:—					
	— 1'5.	— 2'0.	— 2'5.	— 3'0.	— 3'5.	— 4'0.
90	—	+0'511	+0'481	+0'430	+0'365	+0'258
195	—0'259	—0'323	—0'393	—0'474	—0'570	—0'675
224'8	—0'474	—0'556	—0'667	—0'776	—0'905	—1'033
251'3	—0'687	—0'824	—0'965	—1'109	—1'251	—1'394
273	—0'890	—1'046	—1'202	—1'360	—1'517	—1'673
293	—1'068	—1'237	—1'404	—1'572	—1'739	—1'906
318	—1'270	—1'457	—1'643	—1'829	—2'016	—2'204

TABLE III.—HEATS OF ADSORPTION.

Log. amt. Adsorbed.	Q (K. Cal./Mol.).			
	273 — 293°.	251'3 — 273°.	224'8 — 251'3°.	195 — 224'8°.
—0'5	—	—	—	10'0
—0'6	—	—	—	9'7
—0'7	—	—	10'8	9'7
—0'8	—	—	11'5	9'4
—0'9	—	10'7	11'9	—
—1'0	—	11'1	12'3	—
—1'1	—	11'5	—	—
—1'2	13'5	12'0	—	—
—1'3	—	12'4	—	—
—1'4	13'6	12'9	—	—

The heats of adsorption calculated from these values are given in Table III. It will be noted that in general the differential heats fall off as the amount adsorbed increases and as the temperature is lowered. The heats of adsorption between liquid air temperatures and 195° C. could not be derived with any accuracy from the results in Table II., and hence no conclusion can be drawn as to whether or not any part of the adsorption

at these temperatures occurs with heats of adsorption of the order of 0'5-2 K. cal./mol.

Adsorption Iso-bar.

The adsorption isobar is given in Fig. 2 for pressures of 10^{-3} cm. Hg for the range of temperatures 90-293° K. The curve for 10^{-3} cm. Hg is

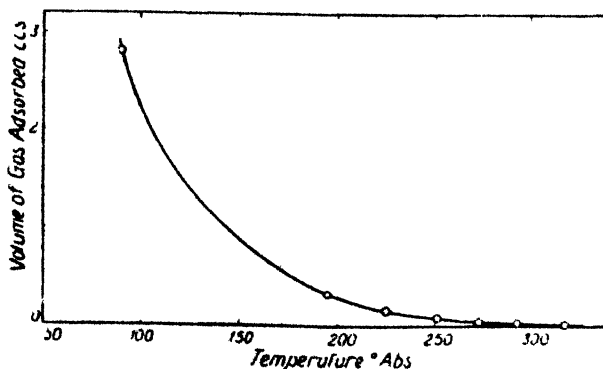


FIG. 2.

very similar in shape. There is no evidence that there is any change in the character of the adsorption between room and liquid air temperatures, except for a gradual decrease in the average heat of adsorption, and there is no discontinuity in the isobars, similar to those obtained by H. S. Taylor

and his co-workers, for many oxides. For example, H. S. Taylor and Strothers^{*} find a minimum at about 200° K. and also two maxima on the adsorption isobar of hydrogen on ZnO. The absence of a discontinuity in the case of carbon monoxide on zinc oxide supports the contention that such discontinuities do not occur in the absence of capillary flow. It is thus doubtful if conclusions drawn from minima on adsorption isobars with regard to the activation energy of adsorption processes are valid unless it has been proved that capillary flow is absent.

Summary.

The heats of adsorption of carbon monoxide on zinc oxide have been determined from the adsorption isotherms over the range of temperatures 195-318° K. and are found to be in agreement with the results obtained in the thermocouple calorimeter.

The adsorption isobar shows no discontinuity and the conclusion is reached that the discontinuities are met with only in the case of adsorbents where capillary flow is present.

Our thanks are due to the Imperial Chemical Industries Limited for a grant for the purchase of apparatus.

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^{*} *J.A.C.S.*, 1934, 588.

REVIEWS OF BOOKS.

Tables of Physical and Chemical Constants and some Mathematical Function. By G. W. C. KAYE and I. H. LABY. Eighth edition. (London: Longmans, Green & Co. Ltd. Pp. 162. Price 14s.)

In the absence of Professor Laby in the antipodes Dr. Kaye has revised these well-known tables, bringing them up-to-date and revising any errors which have been noticed. These tables are too well known to need an extended review. Apart from the inclusion of many more recent values, there has been considerable re-writing in the section on thermometry.

Die Fermente und ihre Wirkungen. By C. OPPENHEIMER. Supplement, Lieferung 1 (Bd. I: Spezieller Teil: Hauptteil VII.-XV., Den Haag: W. Junk, Verlag, 1935. Pp. 160. Price 28s).

The enormous, ever increasing mass of scientific knowledge makes it a difficult task to keep it, so to say, sweet and alive, and prevent it simply accumulating in the issues of periodicals belonging to the past. One has to be most thankful to those men and institutions who have the industry, the energy and the means to concentrate and correlate this wealth of fact and to spread its knowledge outside the narrow range of the pure specialists.

Professor Oppenheimer has become more and more the "Beilstein" of the science of enzymes. His text-book on this subject is so well known that nothing need be said about its value. The supplement which is

beginning to appear is meant to bring the special part of the original work up to date. This first issue treats the esterases (lipases, lecithases, tannases, phosphatases). It commences with a more general, important discussion of modern conceptions of enzyme structure which necessitate the use of a new terminology.

H. F.

Electrolytic Oxidation and Reduction. Monographs on Applied Chemistry, Vol. IX. By S. GLASSSTONE and A. HICKLING. (Pp. ix + 420. Chapman & Hall. 25s. net.)

To the works chemist who has never used electrolytic methods this book opens up new avenues and gives food for thought. The neat processes and the control one can exercise on the progress of the reactions once the fundamental principles are known should have a direct appeal.

To the research worker this book is invaluable, bringing forward as it does the principles of Electrolysis in the light of modern knowledge, thus making a notable addition to existing textbooks. It deals, from a laboratory point of view, equally well with fundamental principles as with experimental data, and the voluminous references enable one to follow any phase of the subject more closely should one so desire. Where conflicting views are held, the pros and cons of each are logically discussed. Conflicting experimental results are pulled into line with theory in such a capable manner that one immediately has confidence that in this work will be found first principles that will hold good.

To the careful reader, imagination will present possibilities of processes not given, because the effective manner in which the data is given for the suppression of undesirable compounds, will open up the way to the production of these compounds when they become desirable.

The title has an advantage and a disadvantage. In the first place it focusses the attention on the fact that in aqueous solution the chief reaction is the electrolysis of water and the chief products Oxygen and Hydrogen. In the second place, it leaves the uninitiated with the impression that these are the only possibilities of electrolysis, although an attempt has been made to remedy this impression by the inclusion of a chapter on substitution as secondary phenomena.

Altogether a well-written and readable book.

R. P. L. B.

Corrosion Resistance of Metals and Alloys. By ROBERT J. MCKAY and R. WORTHINGTON. Pp. 492. (New York: The Reinhold Publishing Corp. London: Chapman & Hall, Ltd. Price 35s. net.)

Mr. R. J. McKay's name has long been associated with the study and combating of corrosion. The present treatise, written in collaboration with Mr. R. Worthington, is assured, therefore, of a very wide welcome.

The first part ("General and Theoretical") is much shorter than and is frankly subservient to the second ("Corrosion Behaviour of Specific Metals and Alloys"). Whilst the author's unconventional treatment of theoretical matters leaves loopholes for criticism, the essential *raison d'être* of the work is represented by the "specific" second part. This

presentation in accessible and assimilable form of data concerning the behaviour of metallic systems in corroding media of various kinds should prove of considerable assistance to many technical workers.

The task of writing such a book is admittedly attended with much difficulty, not the least part of which is associated with the classification of the relevant data. After much consideration of alternatives in both sections, the authors adopt for the specific part a system whereby the information is arranged under the headings of the respective metal systems. Whilst the engineer may prefer to find the behaviour of materials discussed under the particular corroding medium with which he is concerned, any inconvenience is reduced to a minimum by an exceptionally thorough subject index, which constitutes a gratifying feature of the work. The length of the author index further reflects the wideness of the field surveyed.

The style may prove irksome to many, and there is much looseness of expression, as for example the rendering of corroding media indiscriminately as "corrodents," "corrodors," and "corrosives," and stainless steel as "stainless." In all the tables and throughout the text corrosion rates are expressed as "mg. per sq. dm. per day," the reader being left to infer that this refers to loss in weight. Similarly, in Table IV, where factors are given for conversion to "inches per year" and "cm. per year," it is left to inference not only that these values represent depth of penetration (which is sufficiently obvious), but also that the total loss of weight is assumed to be distributed uniformly over the whole area of the specimen, an assumption that is frequently remote from the truth.

The treatment, in general, is thoroughly up-to-date; certain curious lapses have been noted, however. Thus, a brief account of the protection of magnesium and its industrial alloys includes no mention of the selenium process of Bengough and Whitby. A noteworthy omission from the metal systems is that of silver and its alloys which now find many important applications in chemical engineering. Sectional bibliographies at the end of each chapter, supplement usefully the information given in the text, and the number of references so included is extremely large. The production and printing is in every way satisfactory.

W. H. J. V.

Coal: Its Constitution and Uses. By W. A. BONE and G. W. HUMUS; with a chapter on fuel economy and heat transmission in industrial furnaces by R. J. SARJANT. Pp. vii + 631. (Longmans, Green & Co., 1936. 25s.)

During the eighteen years which have passed since Professor Bone's monograph on coal was published, there have been important developments in coal chemistry, and in the application of coal as an industrial raw material. The present book follows the same general lines as its predecessor, but the task of bringing all the material in it up to date has involved much more than mere revision, and many entirely new sections now appear.

The introductory chapters are concerned with the coal industry from the economic side, and are followed by a description of the geology of the coal measures, and the mechanism of changes in the series lignin—peat—

coal. The different systems of classification of coals are reviewed, with particular reference to microscopic examination of bituminous types. The chemical constitution of coal is then considered, as revealed by the three alternative methods of attack: thermal decomposition, solvent extraction and oxidation. The chemistry of coal combustion is discussed in connection with such problems as smoke abatement, firing of boilers, and the use of pulverised fuel. This order of treatment leads naturally to a series of chapters on the carbonisation of coal, together with an account of the manufacture of water-gas and the complete gasification of coal. Fuel problems connected with the iron and steel industries are next examined, and the use of coal for power production, and for domestic heating, is considered in subsequent sections. A description of the recently established coal hydrogenation process is included and the phenomena of surface combustion are also reviewed. The final chapter, contributed by Dr. Sarjant, is concerned with fuel economy and heat transfer in industrial furnaces.

The book should appeal to a wide range of readers, in both academic and industrial circles, as a thorough and authoritative summary of information now available. Much material is included, from the laboratories of the Imperial College of Science and Technology, which has not been published elsewhere, and many suggestions are made with the intention of stimulating further research. Interest will naturally be focussed on those sections with which the authors have had so many years intimate contact, such as the chemistry of coal, the phenomena of combustion and the reactions of the blast furnace. At the same time the more technical chapters provide a good picture of the relation of industrial processes to coal itself, although they are inevitably brief in their treatment and rightly exclude any discussion of by-products.

The inclusion of a bibliography at the end of most of the chapters increases the ease of reference to original publications. The printing and binding of the book have been most efficiently carried out, and the illustrations on the whole are excellent; in a few cases (e.g. Figs. 42, 86, and 126) the lettering has been so reduced in size as to be illegible, and the drawings indicating the operation of a water-gas plant are too small to be useful.

R. H. G.

Die Thermodynamik einheitlicher Stoffe und binärer Gemische, mit Anwendungen auf verschiedene physikalisch-chemische Probleme.

By Dr. J. J. VAN LAAR. (P. Noordhoff, N.V., Groningen-Batavia, 1935. Pp. viii + 379. Price 12 gld., Bound 13.50 gld.)

Dr. van Laar develops in this treatise, which is divided into two parts as indicated by the title, the general theory of two-phase equilibria of simple substances and binary systems. Both books start with a brief discussion of van der Waals' general equation of state; the first deals with the functional dependence of a and b on volume and temperature and, in the second, the dependence on the molar concentration is discussed; the fundamental thermodynamical relations are then introduced. By combining the two theories a detailed analysis of the two-phase equilibria not too near the critical region (gas-liquid) is given. The mode of approach

is typical of the Dutch school of thermodynamics, which carefully correlates the deviations from the ideal laws (e.g. Raoult's law) with the higher terms with x^3 in the molar thermodynamical potentials, which in turn result from the a and b of the van der Waals' equation. It is interesting to note how the use of these more general expressions leads to a classification of the vapour pressure curves for binary liquids and of the curves of co-existence for two liquid phases (critical miscibility).

The author has successfully demonstrated the main theorems in a concise way which allows a very clear perception of the theoretical framework. He has added, where it appeared of interest, a critical examination of less exact conceptions (e.g. in relation to Dalton's law) and even of erroneous theoretical representation (e.g. in relation to the osmotic pressure). Furthermore, repeated warnings are given against rash conclusions as to chemical association from deviations from the ideal laws. If association does occur, independent evidence is always absolutely necessary.

In many parts numerical applications of the theoretical deductions are given, in which respect the present work differs from the classic treatise by van der Waals-Kohnstamm. Special mention may also be made of the comprehensive and critical discussion of the melting-, evaporation- and sublimation-curves for all the elements, in which the experimental results are checked.

The theory of strong electrolytes is mentioned mainly in connection with two-phase equilibria. The author favours the Ghosh theory; however, his theoretical objection against the Debye-Hückel theory is not very conclusive, whereas the temperature independence of the Ghosh's "average" distance is not discussed.

In two respects this work might gain in value. The statement that the "constants" a and b do vary with volume and temperature is amply justified. It would seem that because of the importance of these quantities a more extensive analysis of their connection with the molecular constants, i.e. the molecular volumes and the molecular attractive and repulsive forces, is desirable. Secondly, the section on specific heats might have been a little more detailed, since modern spectroscopy and statistical theory have given such detailed and accurate information about rotational and vibrational states.

Apart from these two criticisms this treatise is an important addition to the series of monographs of the Dutch School, and needs no further recommendation to all those who are acquainted with the author's earlier works. The volume is excellently printed and produced and contains but few misprints.

D. McG.

Transactions of the Faraday Society.

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